Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Selective Homo- and Cross-Desilacoupling of Aryl and Benzyl Primary Silanes Catalyzed by Barium Complex

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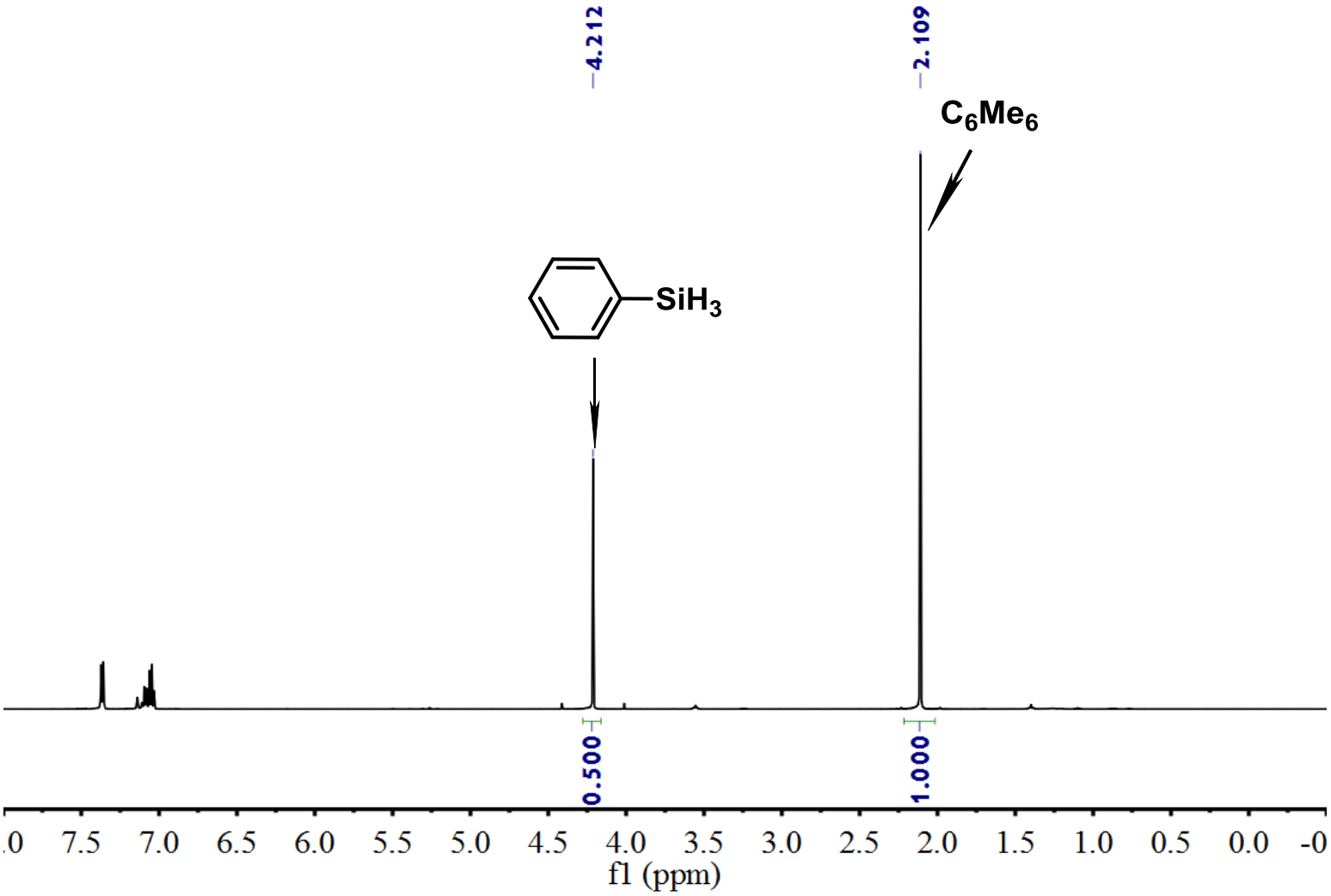

Figure S1. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of $PhSiH_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

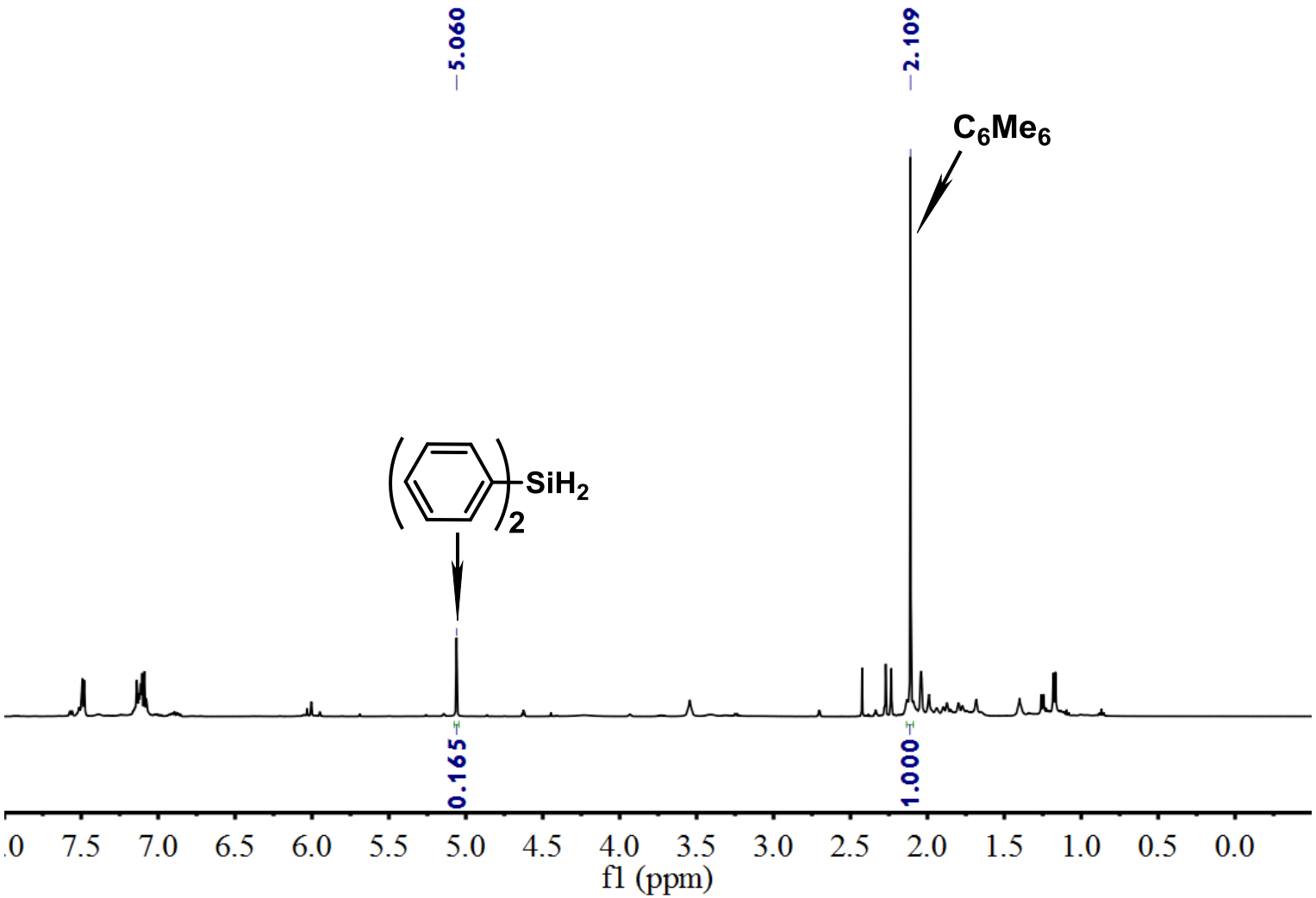

Figure S2. Quantitative ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 1) (500 MHz, C_6D_6, 25 ^{o}C).

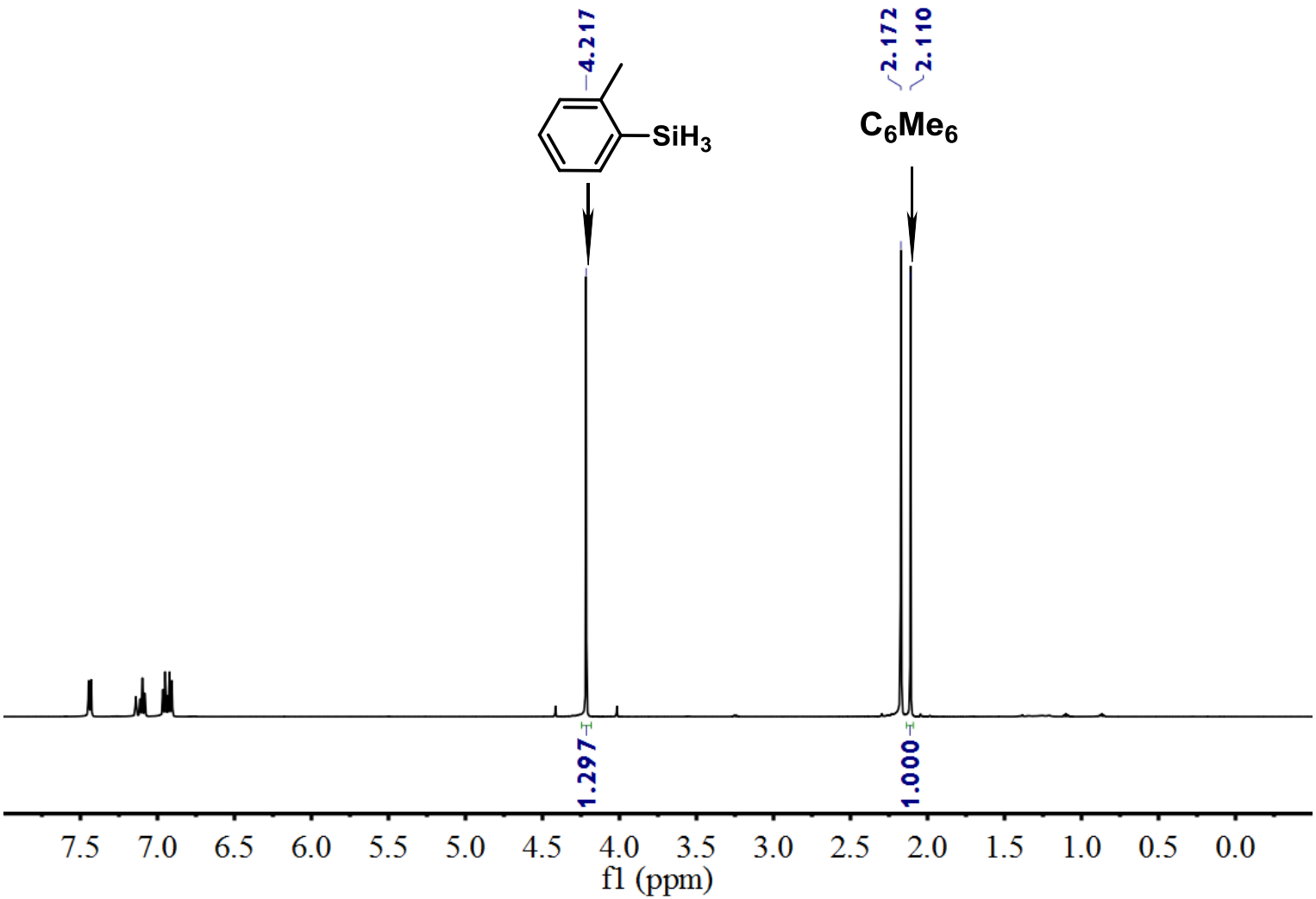

Figure S3. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 2-Me-PhSiH$_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

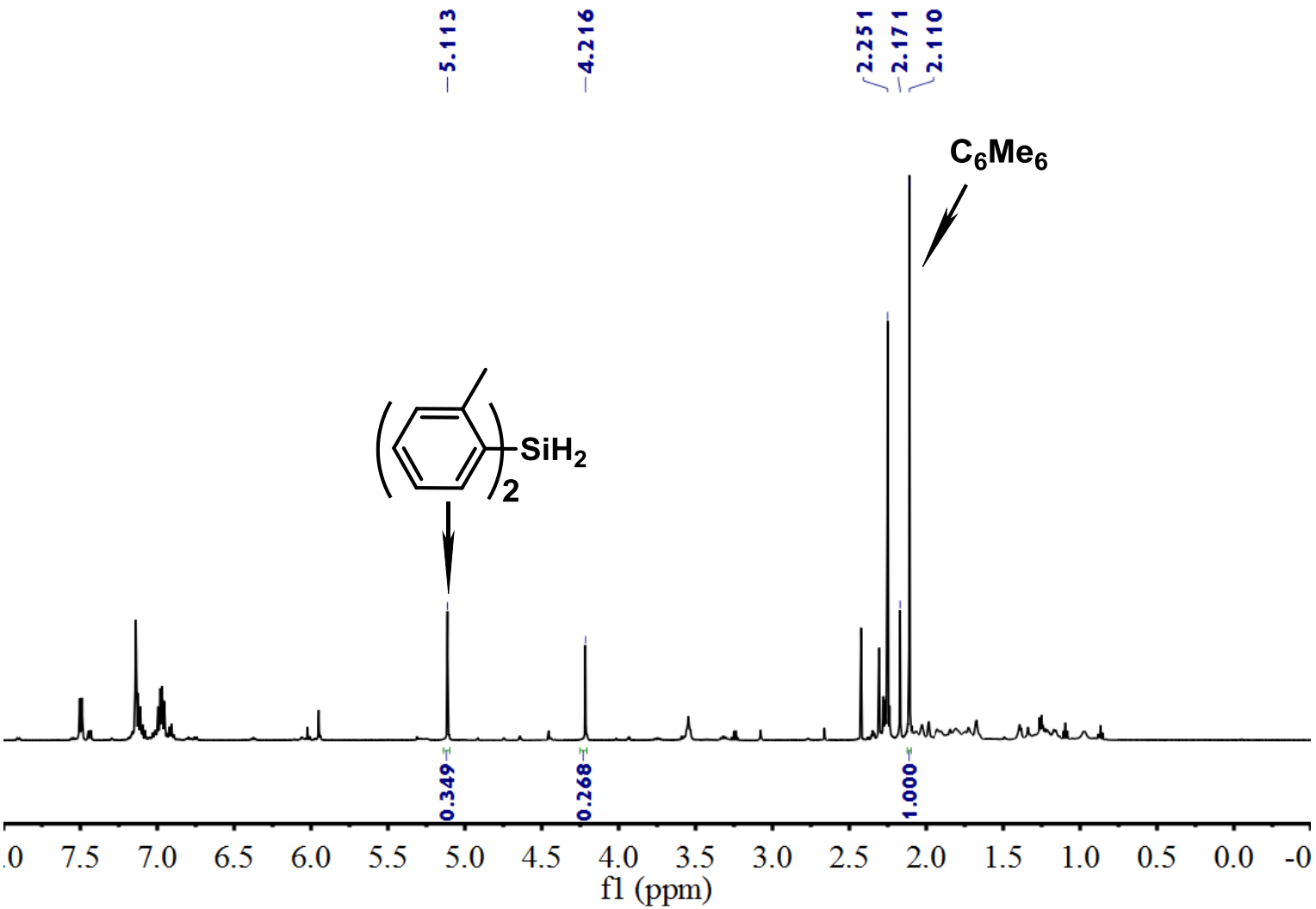

Figure S4. Quantitative ^{1}H NMR spectrum of the products of redistribution of 2-Me-PhSiH$_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 2) (500 MHz, C_6D_6, 25 ^{o}C).

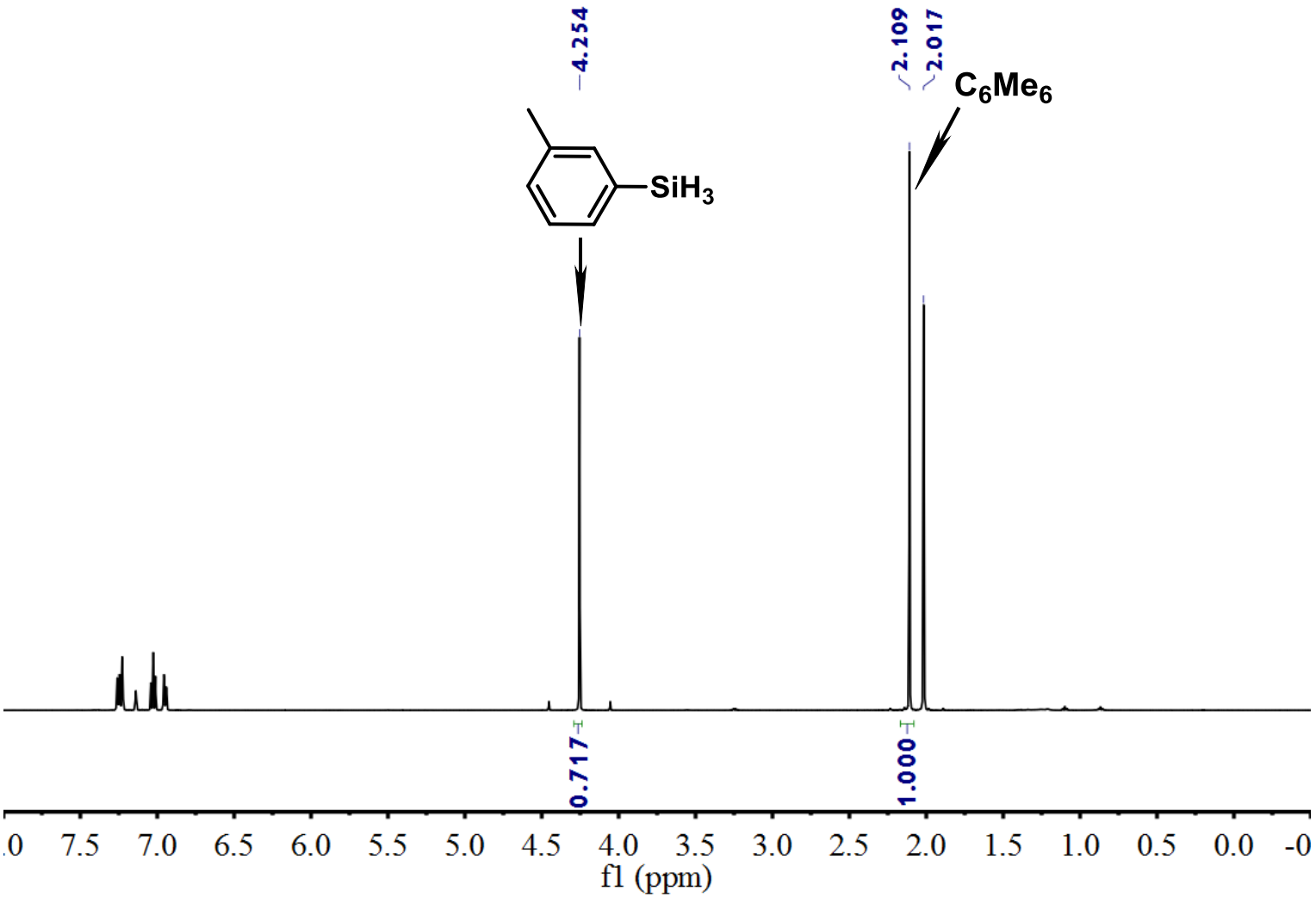

Figure S5. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 3-Me-$PhSiH_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

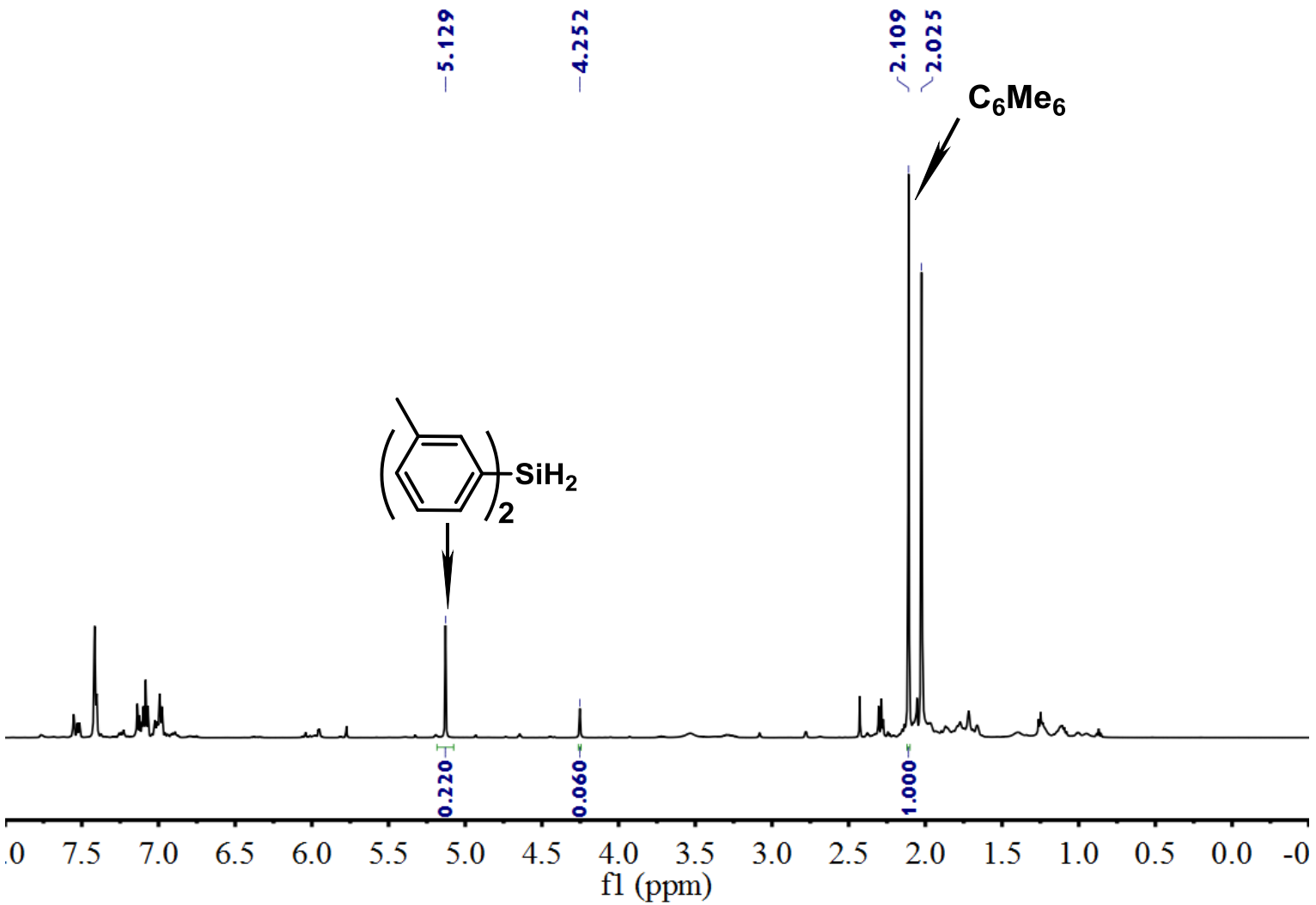

Figure S6. Quantitative ^{1}H NMR spectrum of the products of redistribution of 3-Me-PhSiH$_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 3) (500 MHz, C_6D_6, 25 ^{o}C).

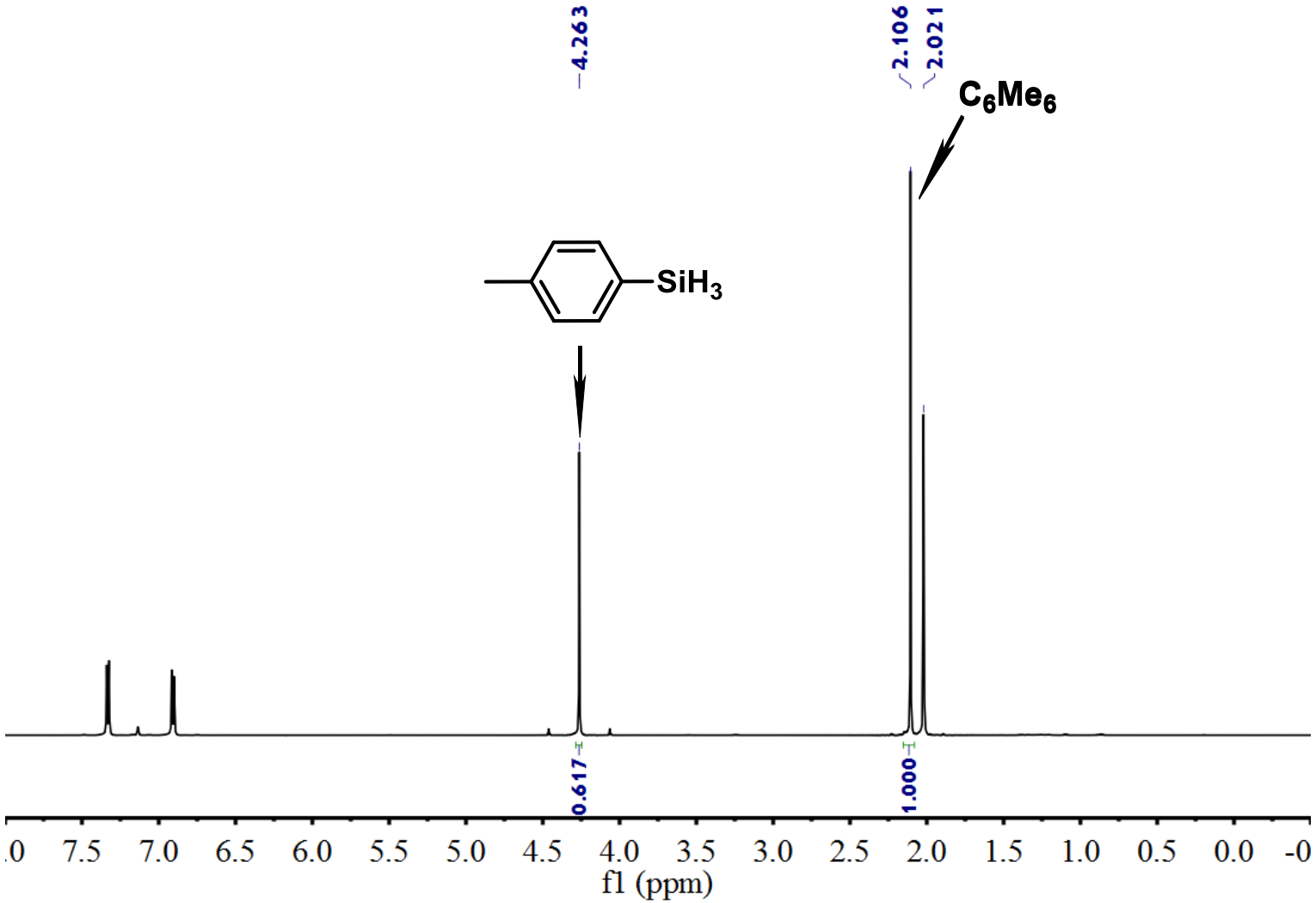

Figure S7. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Me-PhSiH$_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

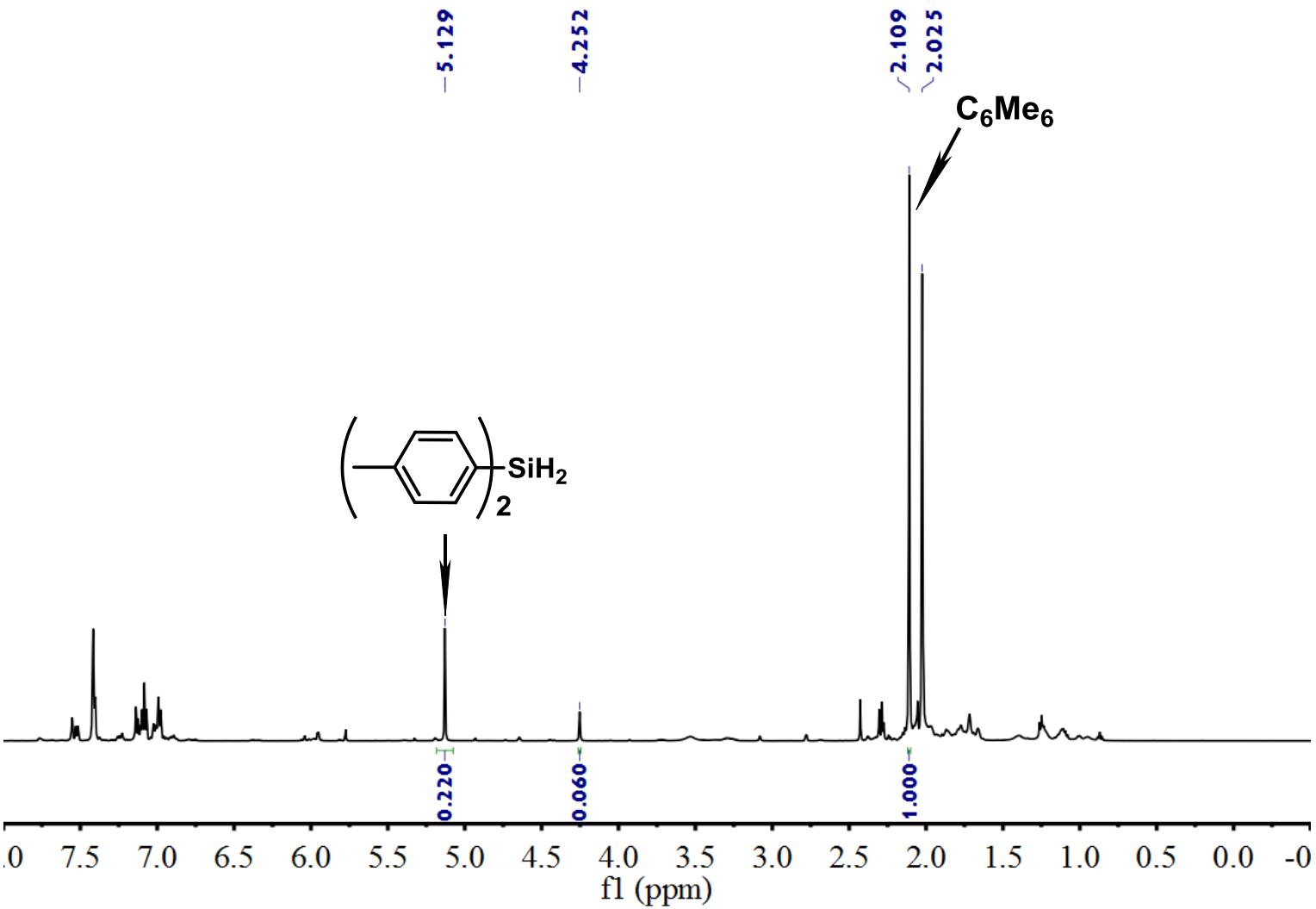

Figure S8. Quantitative ^{1}H NMR spectrum of the products of redistribution of 4-Me-PhSiH$_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 4) (500 MHz, C_6D_6, 25 ^{o}C).

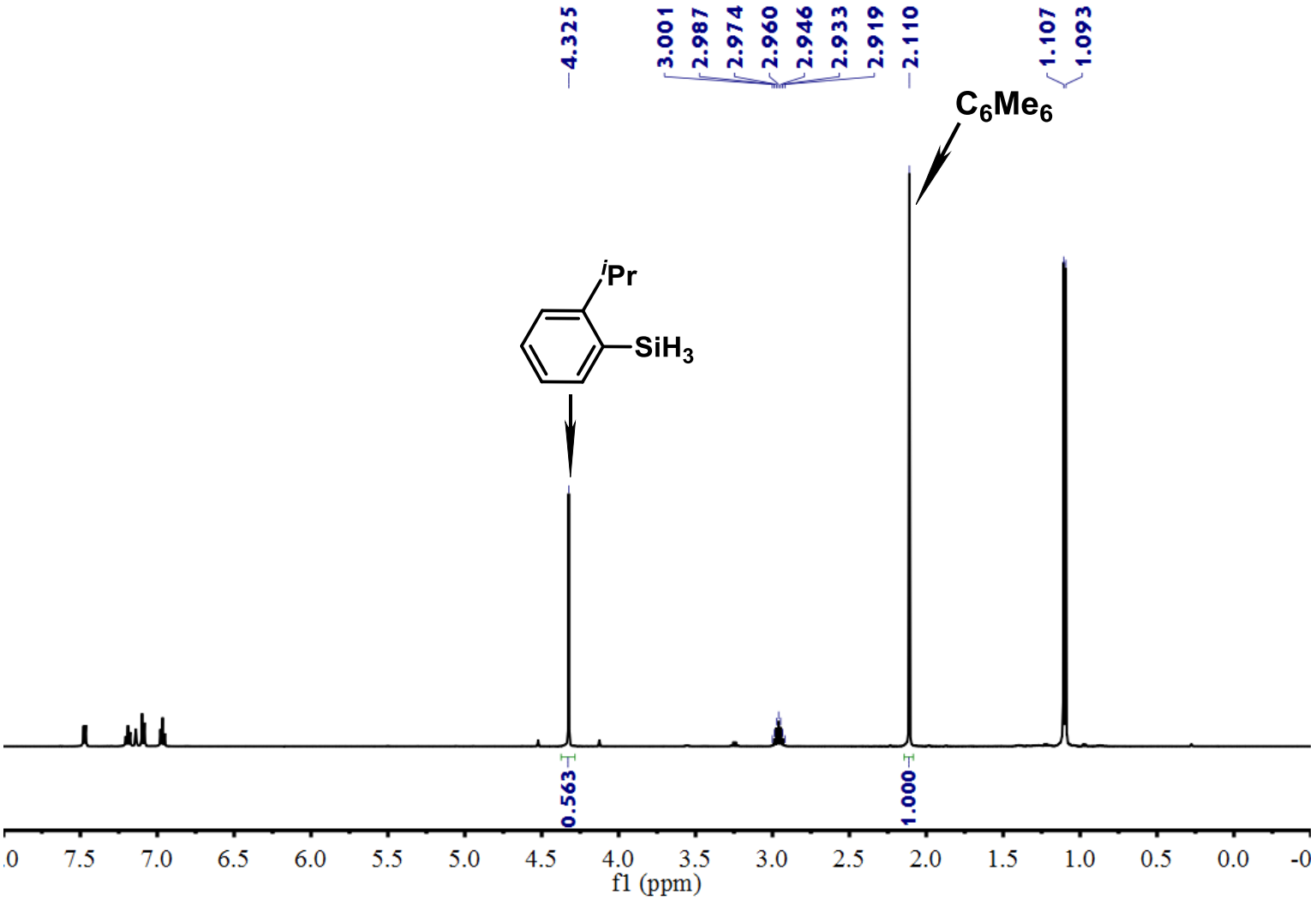

Figure S9. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 2-^{i}Pr-PhSiH$_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

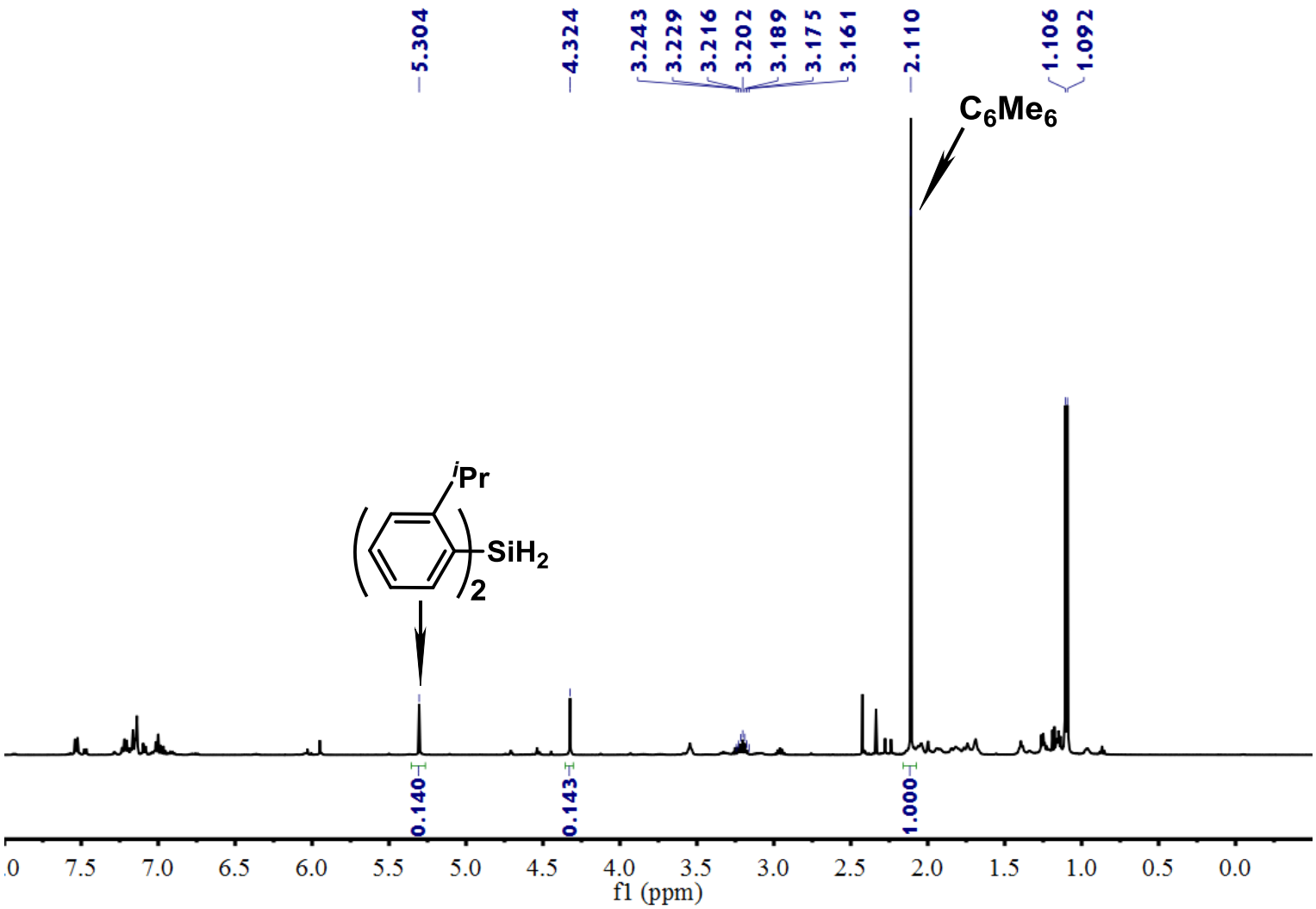

Figure S10. Quantitative ^{1}H NMR spectrum of the products of redistribution of 2-^{i}Pr-PhSiH$_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 5) (500 MHz, C_6D_6, 25 ^{o}C).

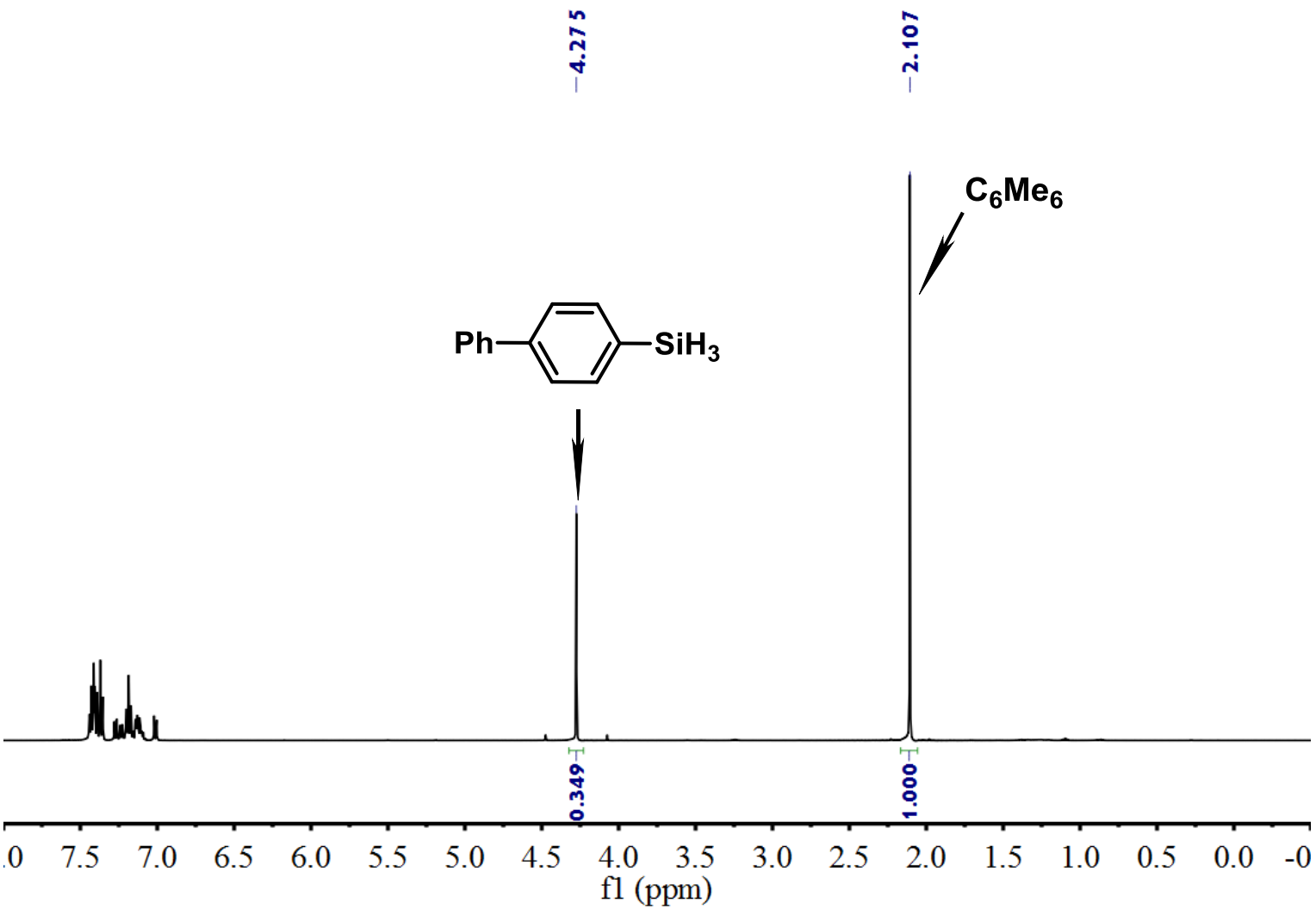

Figure S11. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Ph-$PhSiH_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

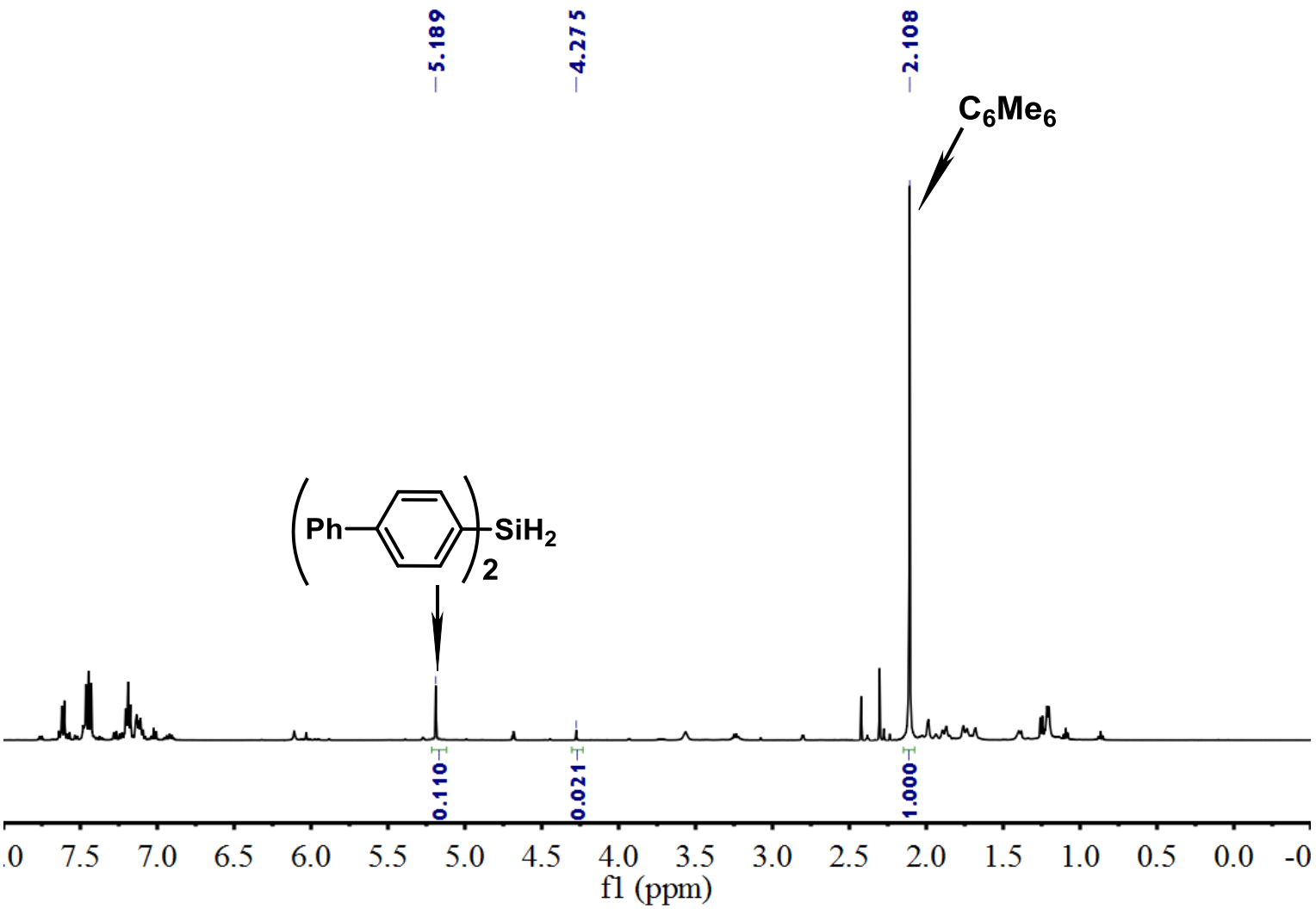

Figure S12. Quantitative ^{1}H NMR spectrum of the products of redistribution of 4-Ph-$PhSiH_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 7) (500 MHz, C_6D_6, 25 ^{o}C).

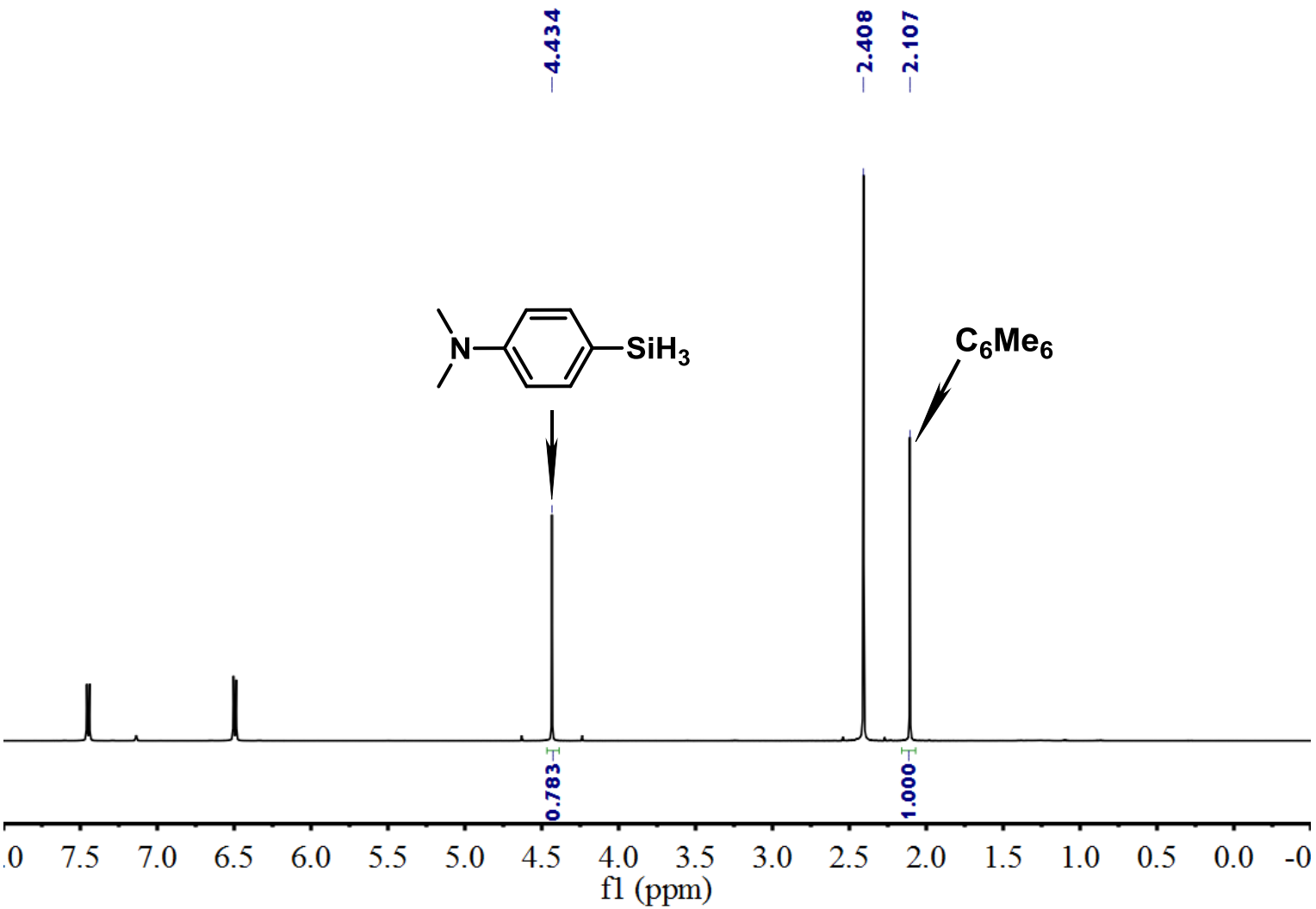

Figure S13. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-NMe_2-$PhSiH_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

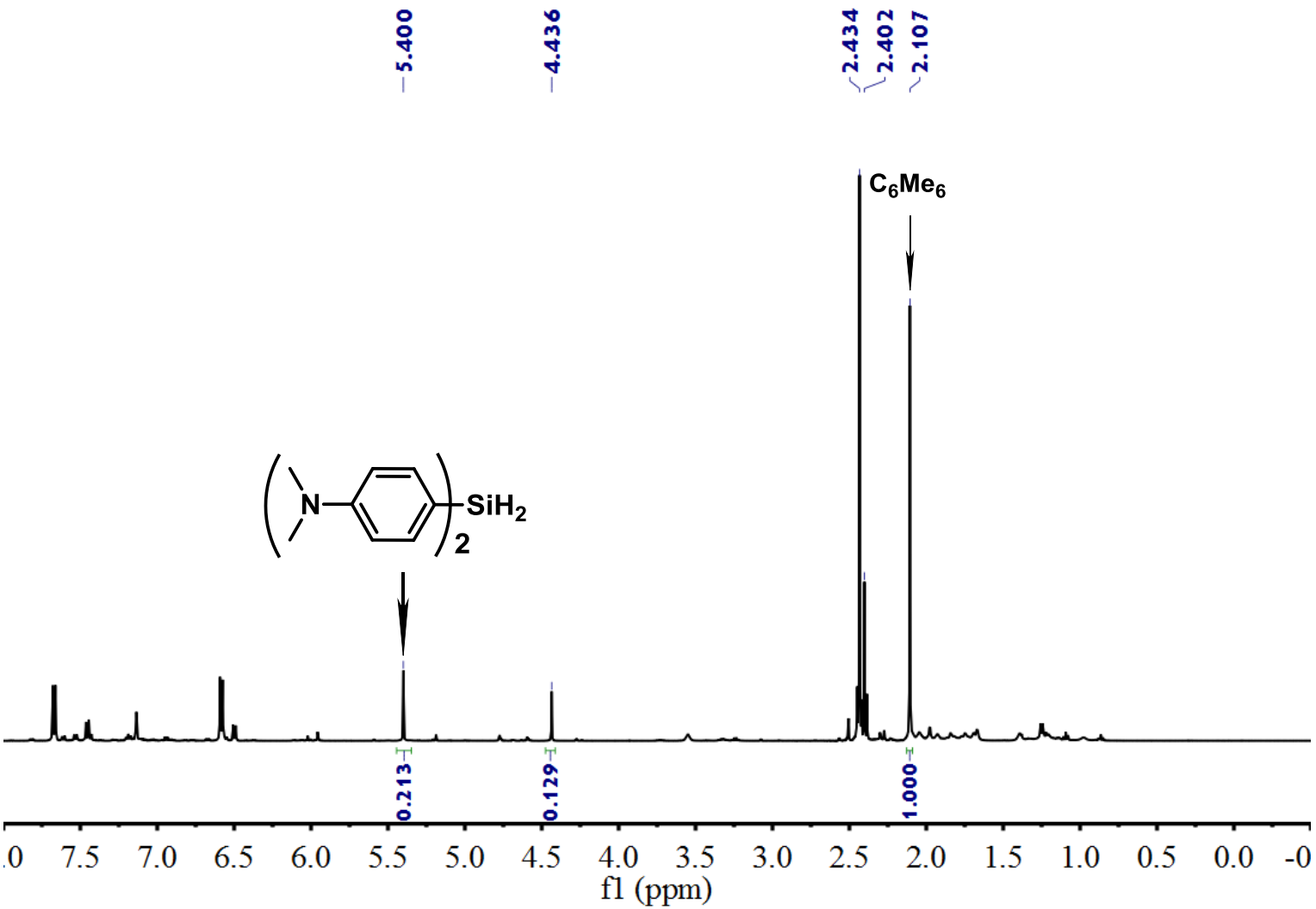

Figure S14. Quantitative ^{1}H NMR spectrum of the products of redistribution of 4-NMe_2-$PhSiH_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 8) (500 MHz, C_6D_6, 25 ^{o}C).

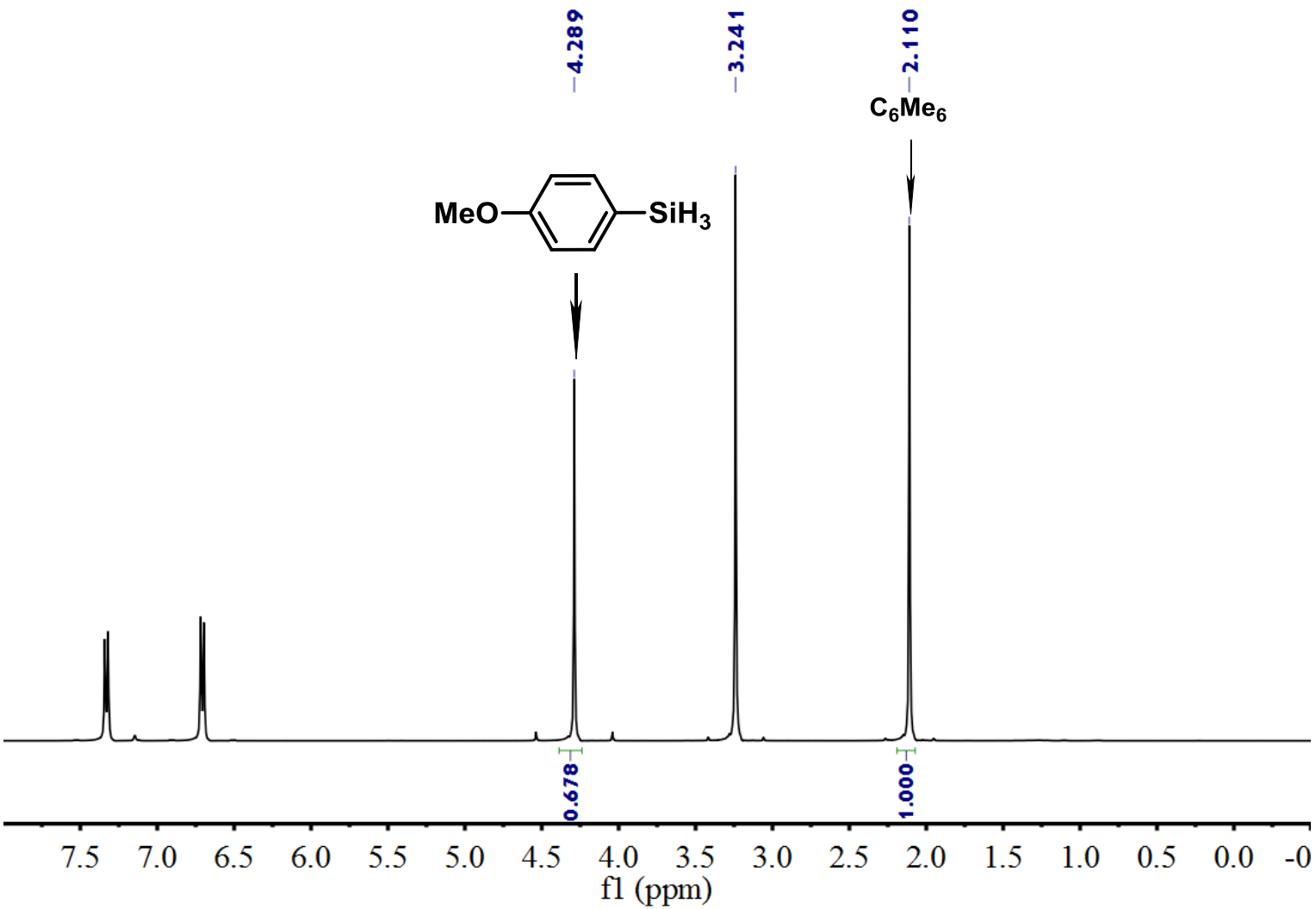

Figure S15. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-MeO-PhSiH$_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

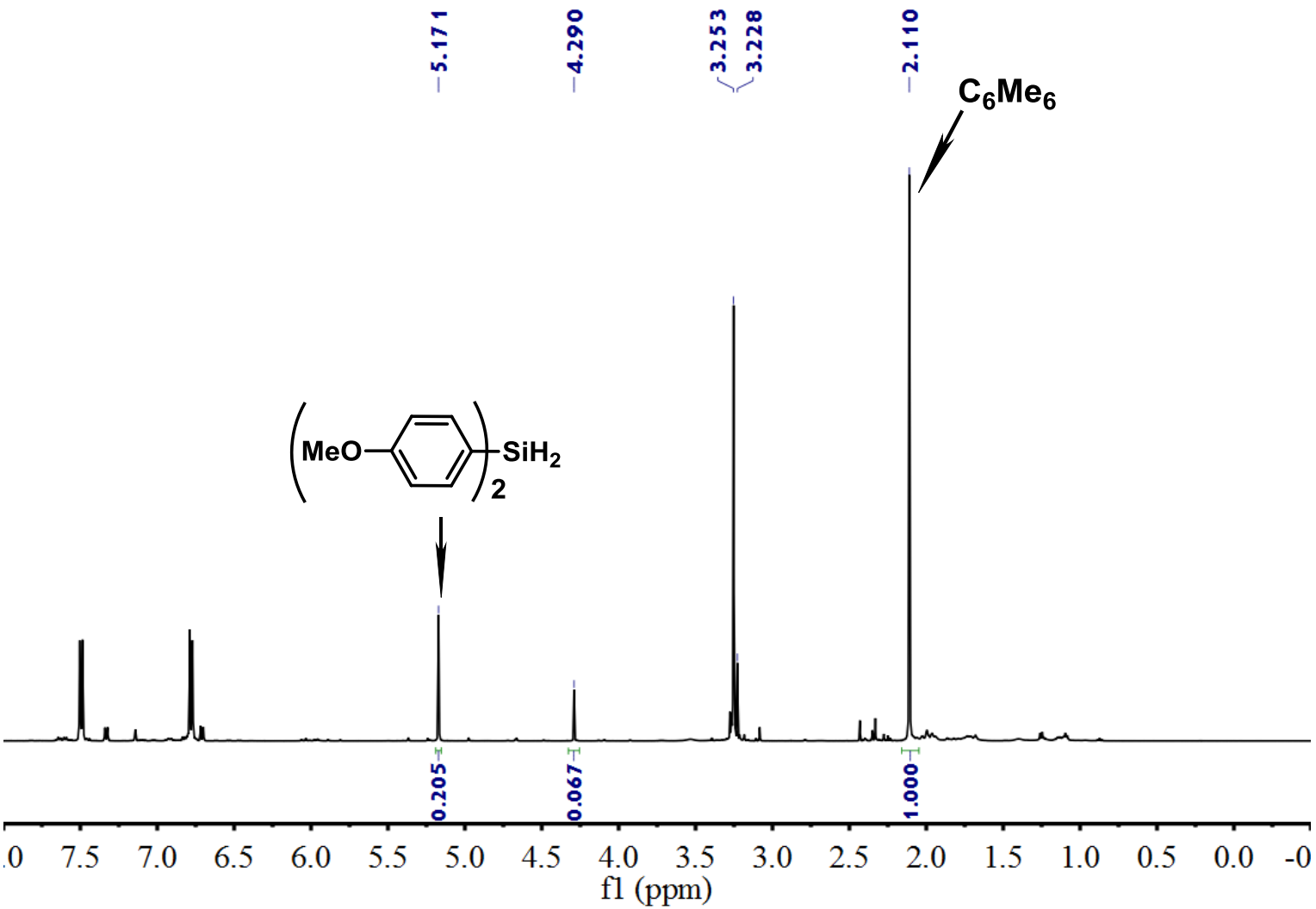

Figure S16. Quantitative ^{1}H NMR spectrum of the products of redistribution of 4-MeO-PhSiH$_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 9) (500 MHz, C_6D_6, 25 ^{o}C).

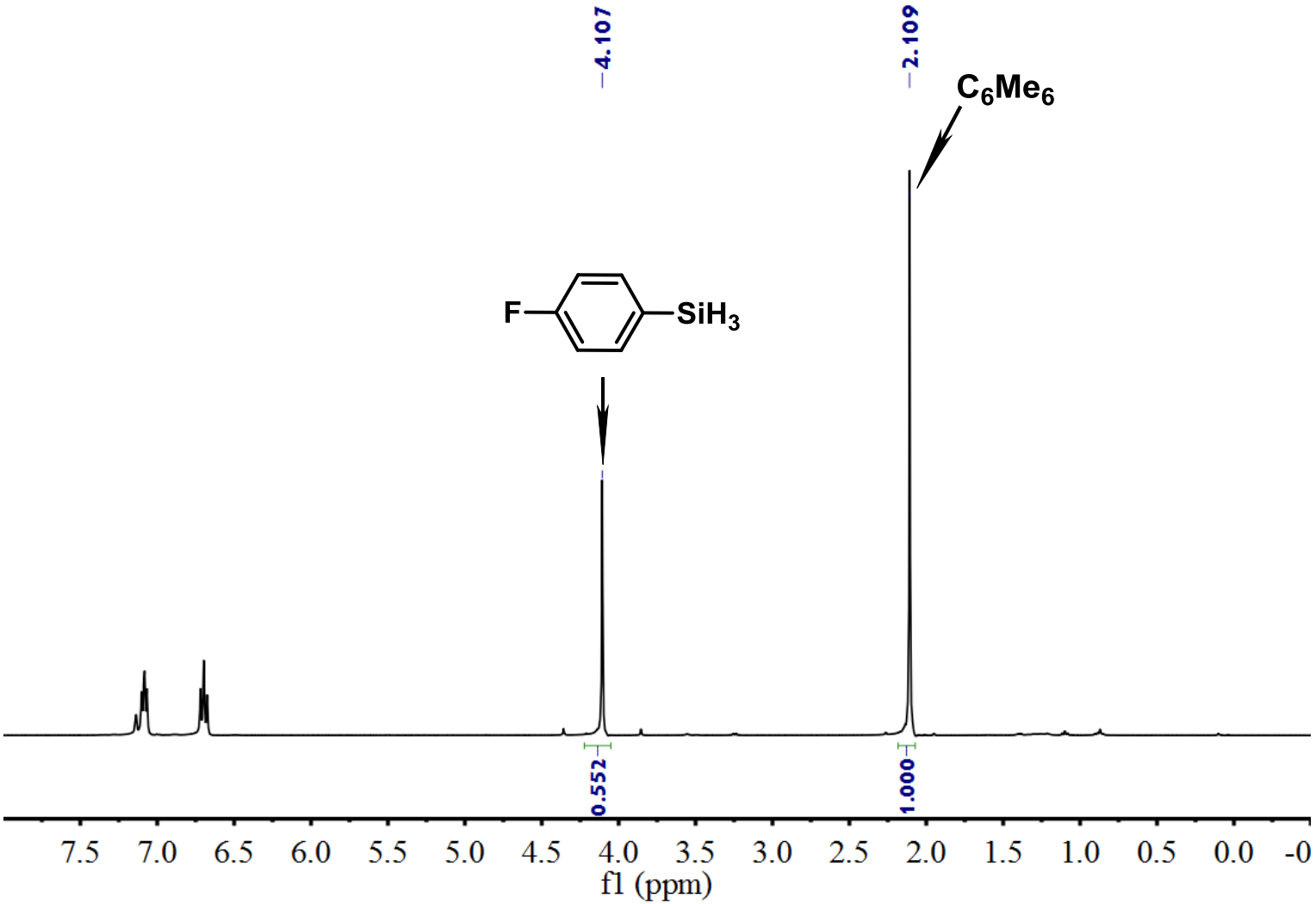

Figure S17. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-F-PhSiH$_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

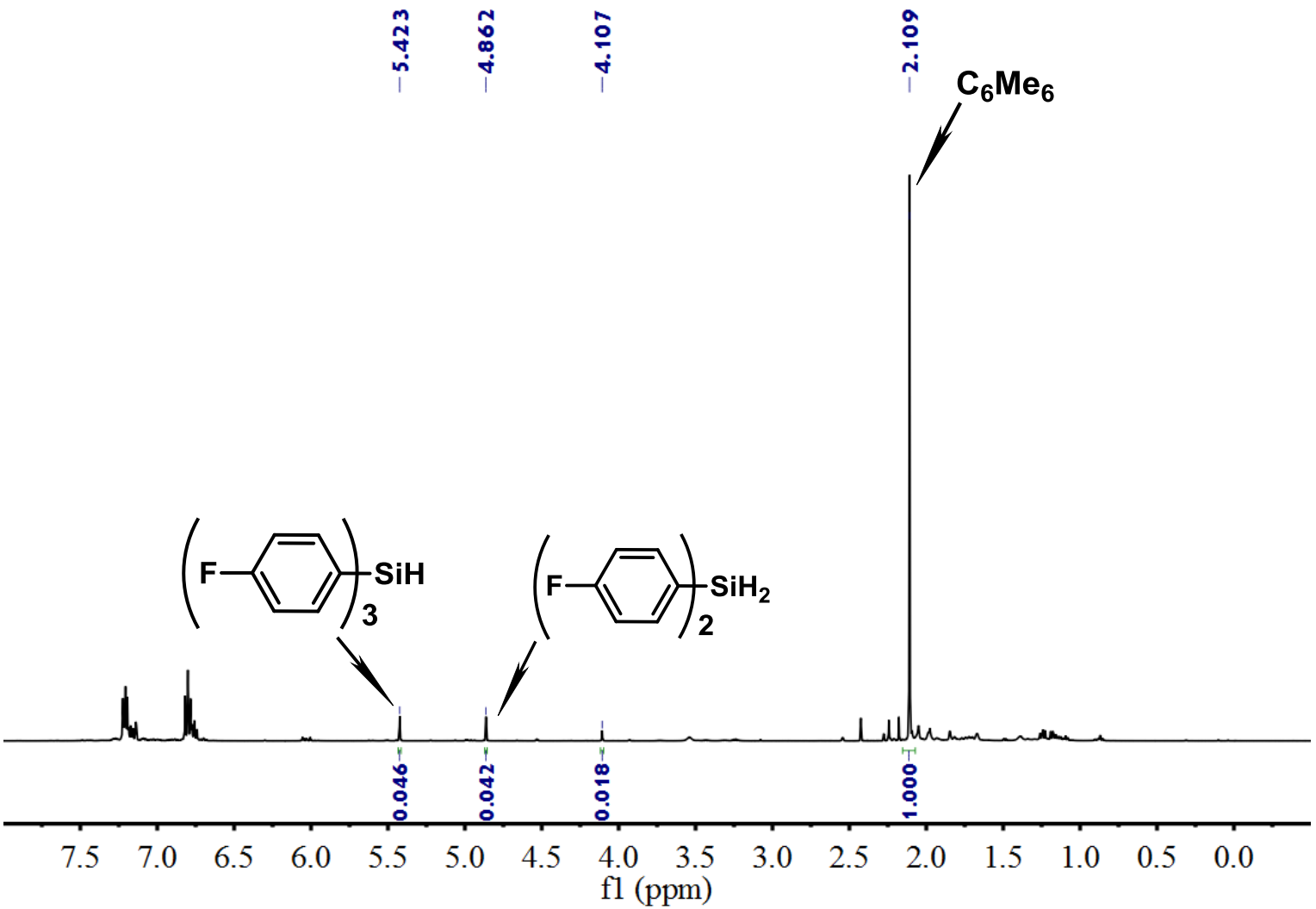

Figure S18. Quantitative ^{1}H NMR spectrum of the products of redistribution of 4-F-PhSiH$_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 10) (500 MHz, C_6D_6, 25 ^{o}C).

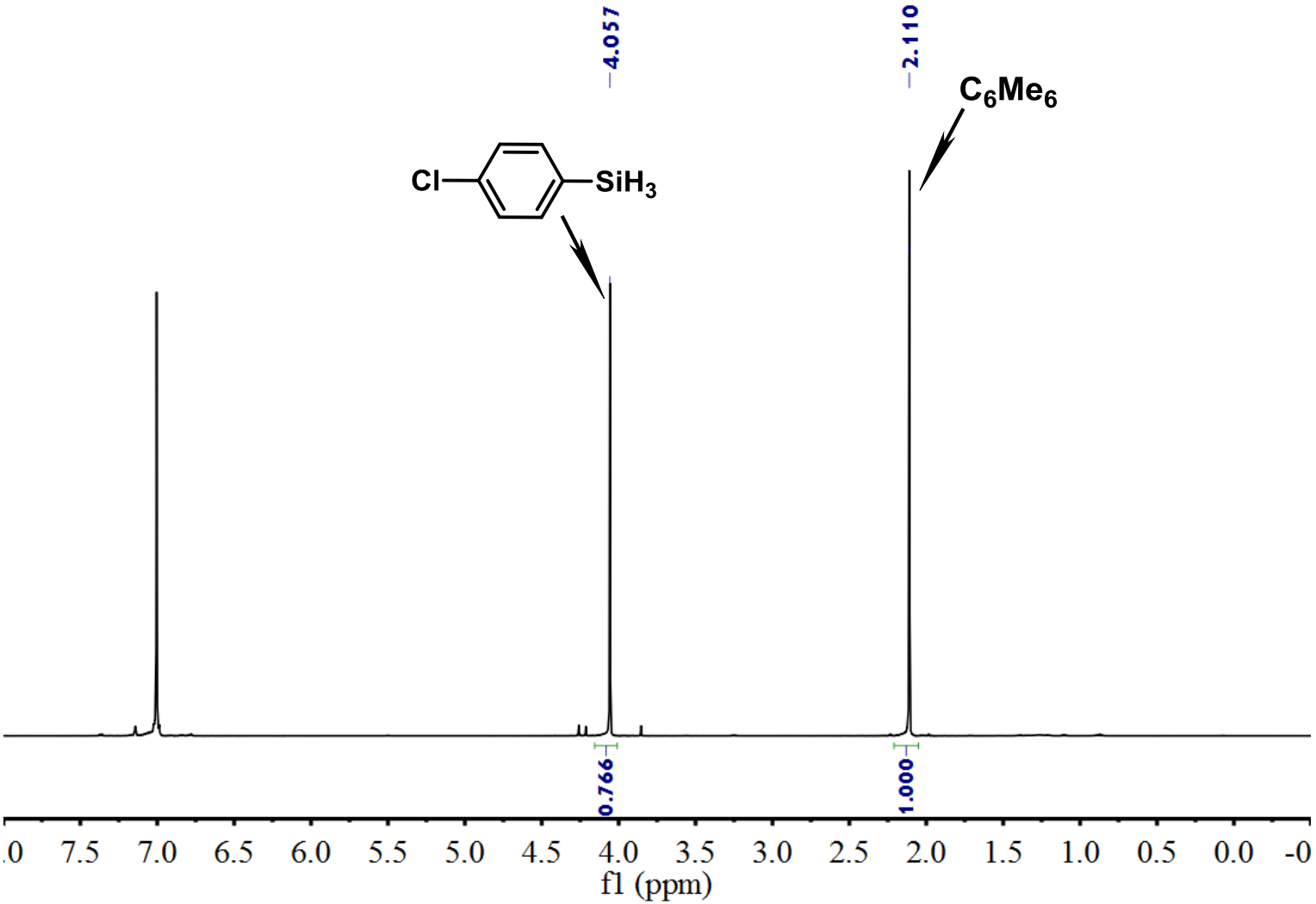

Figure S19. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Cl-PhSiH$_3$ for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

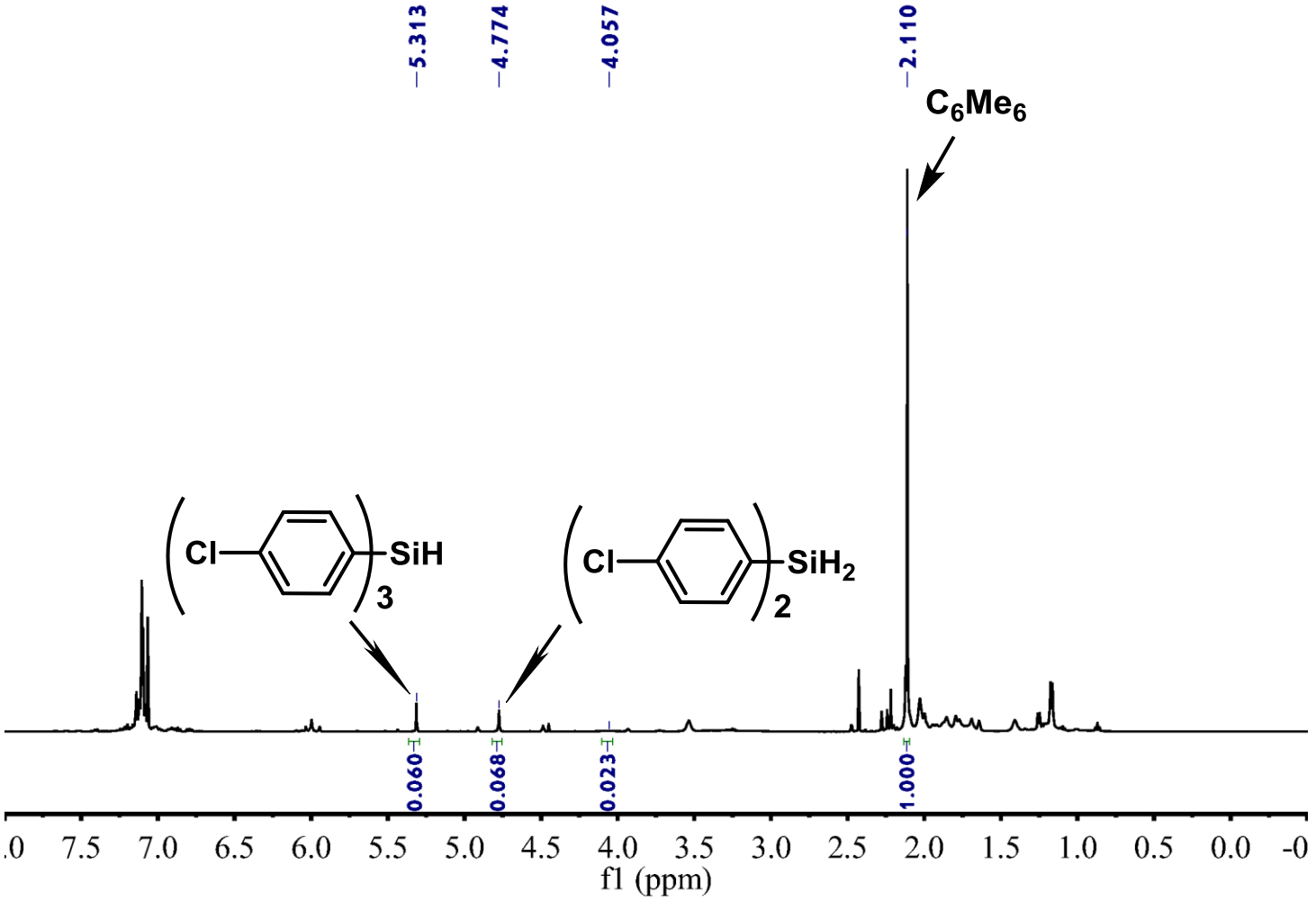

Figure S20. Quantitative ^{1}H NMR spectrum of the products of redistribution of 4-Cl-PhSiH$_3$ catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 11) (500 MHz, C_6D_6, 25 ^{o}C).

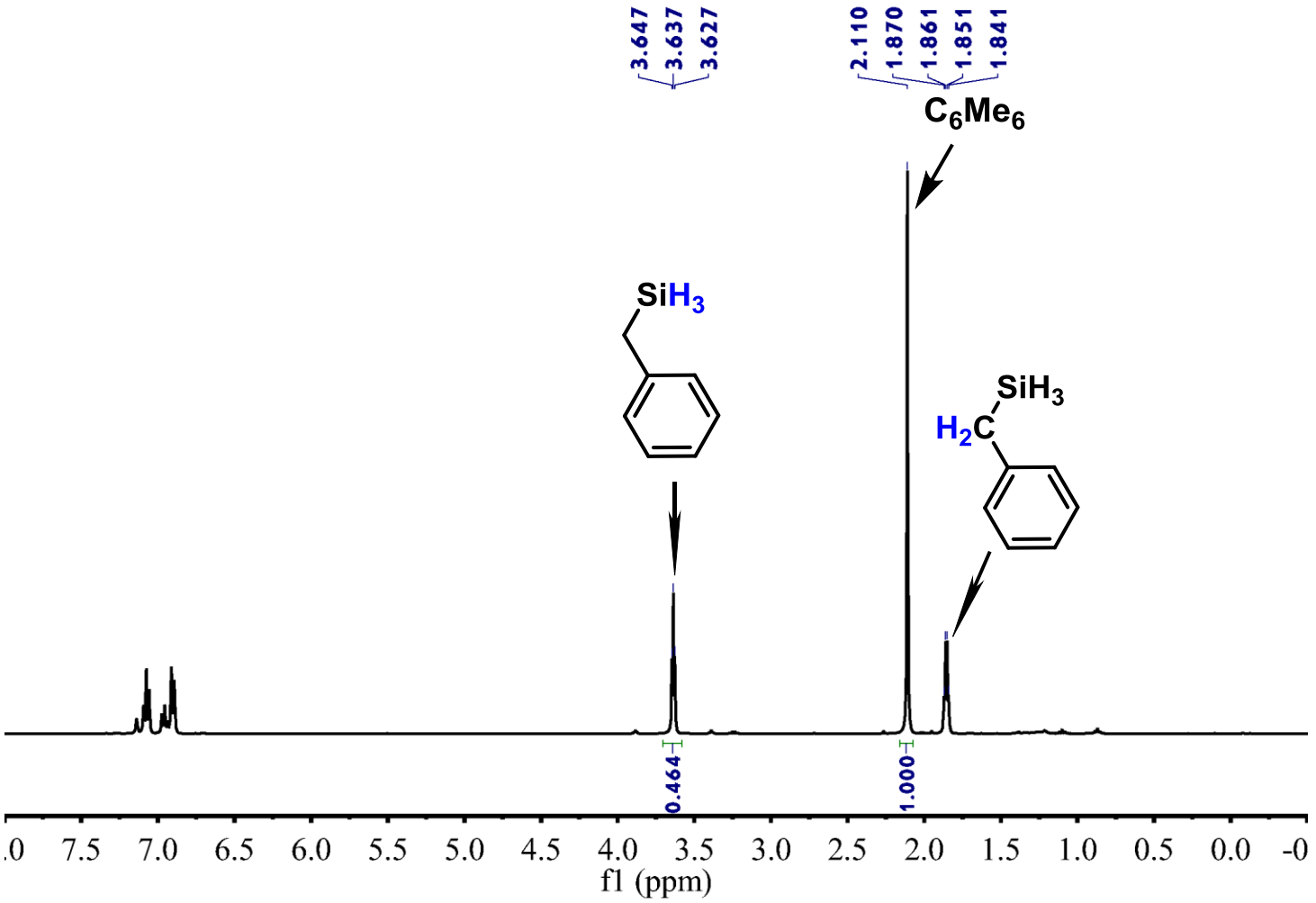

Figure S21. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane for the catalytic redistribution study with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

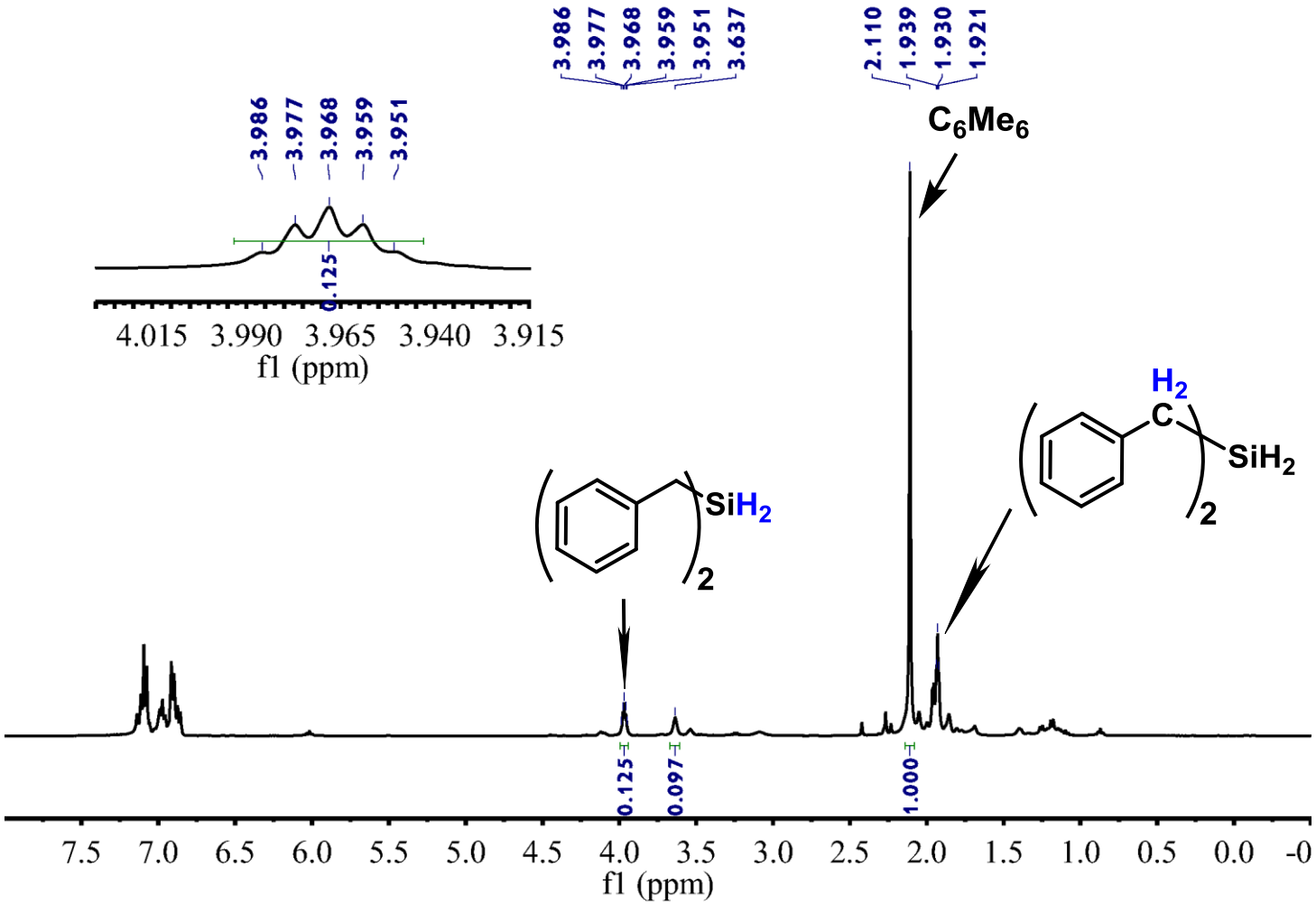

Figure S22. Quantitative ^{1}H NMR spectrum of the products of redistribution of benzylsilane catalyzed by 5 mol% of **1** at r.t. in 10 min (Table 1, entry 13) (500 MHz, C_6D_6, 25 ^{o}C).

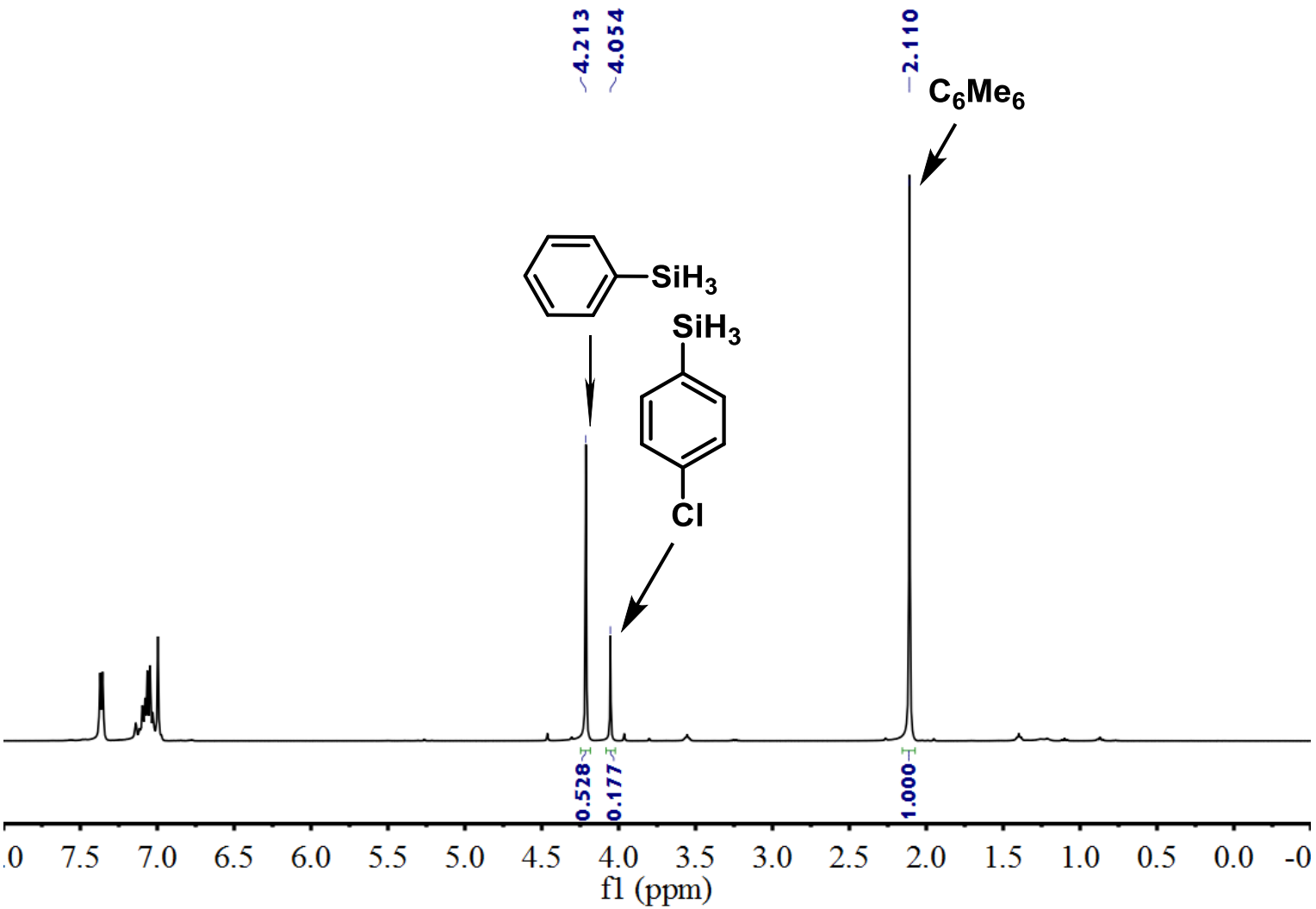

Figure S23 Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Cl-$PhSiH_3$ and $PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

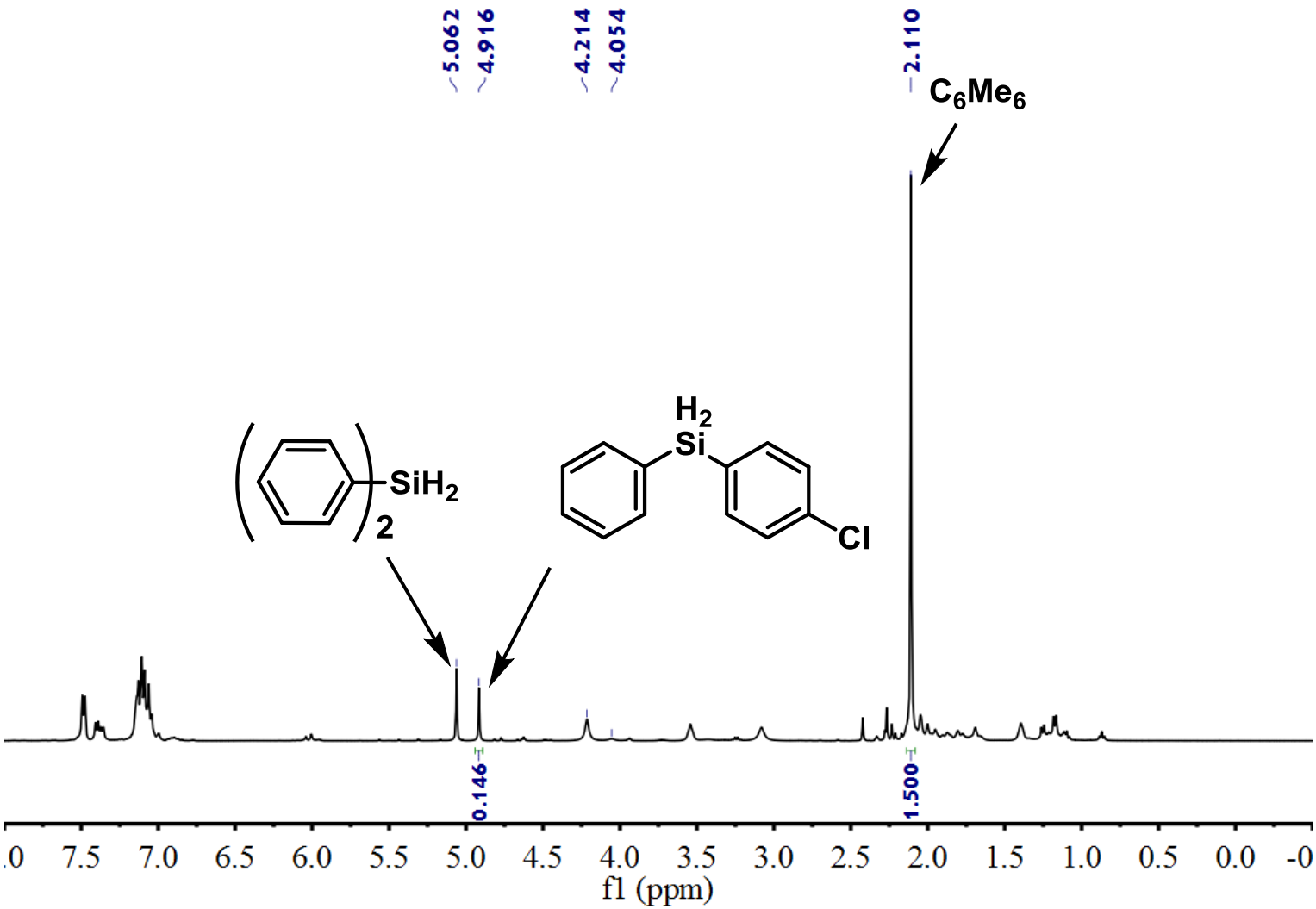

Figure S24. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-Cl-PhSiH$_3$ and PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

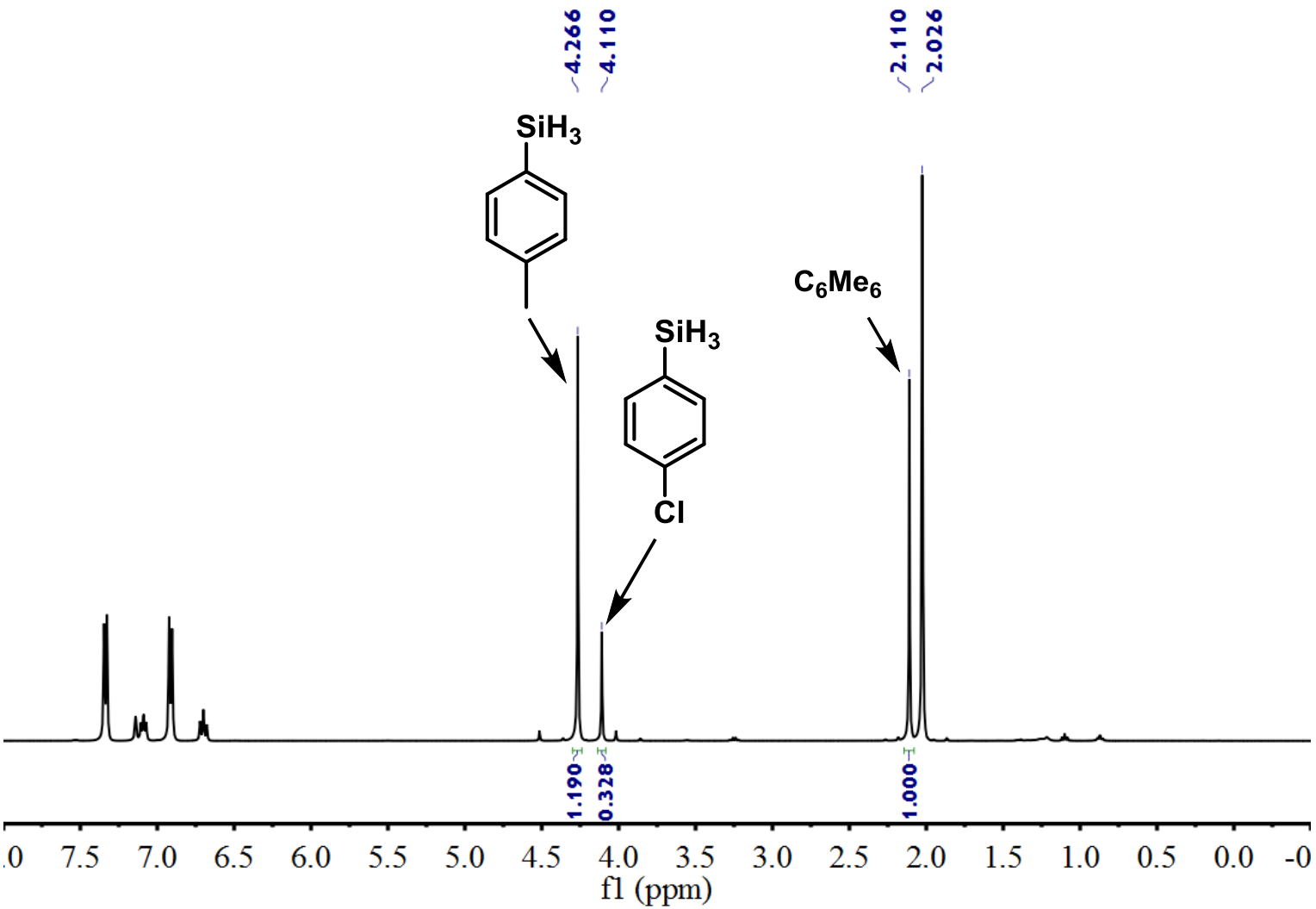

Figure S25. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Cl-PhSiH$_3$ and 4-Me-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

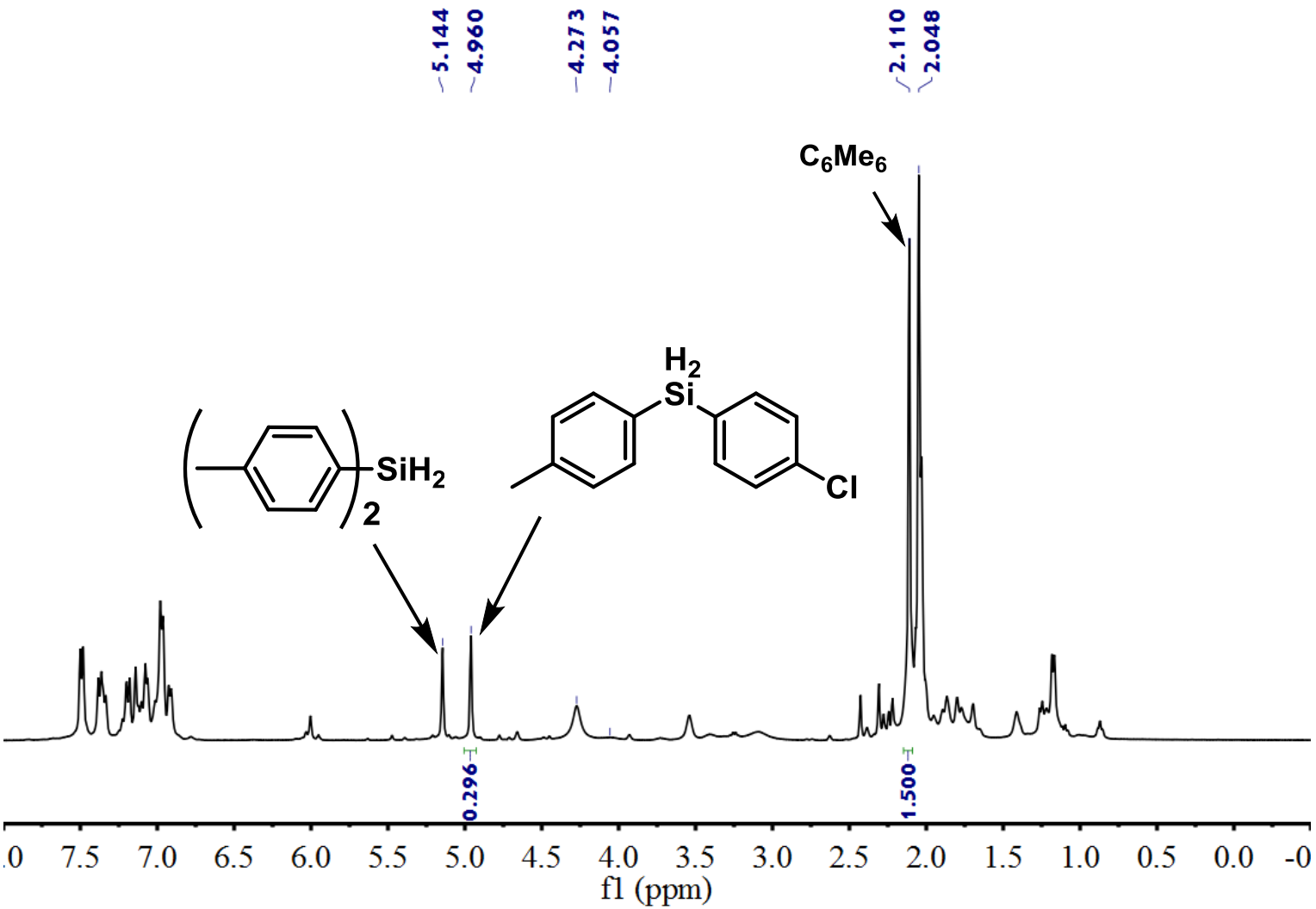

Figure S26. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-Cl-PhSiH$_3$ and 4-Me-PHSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

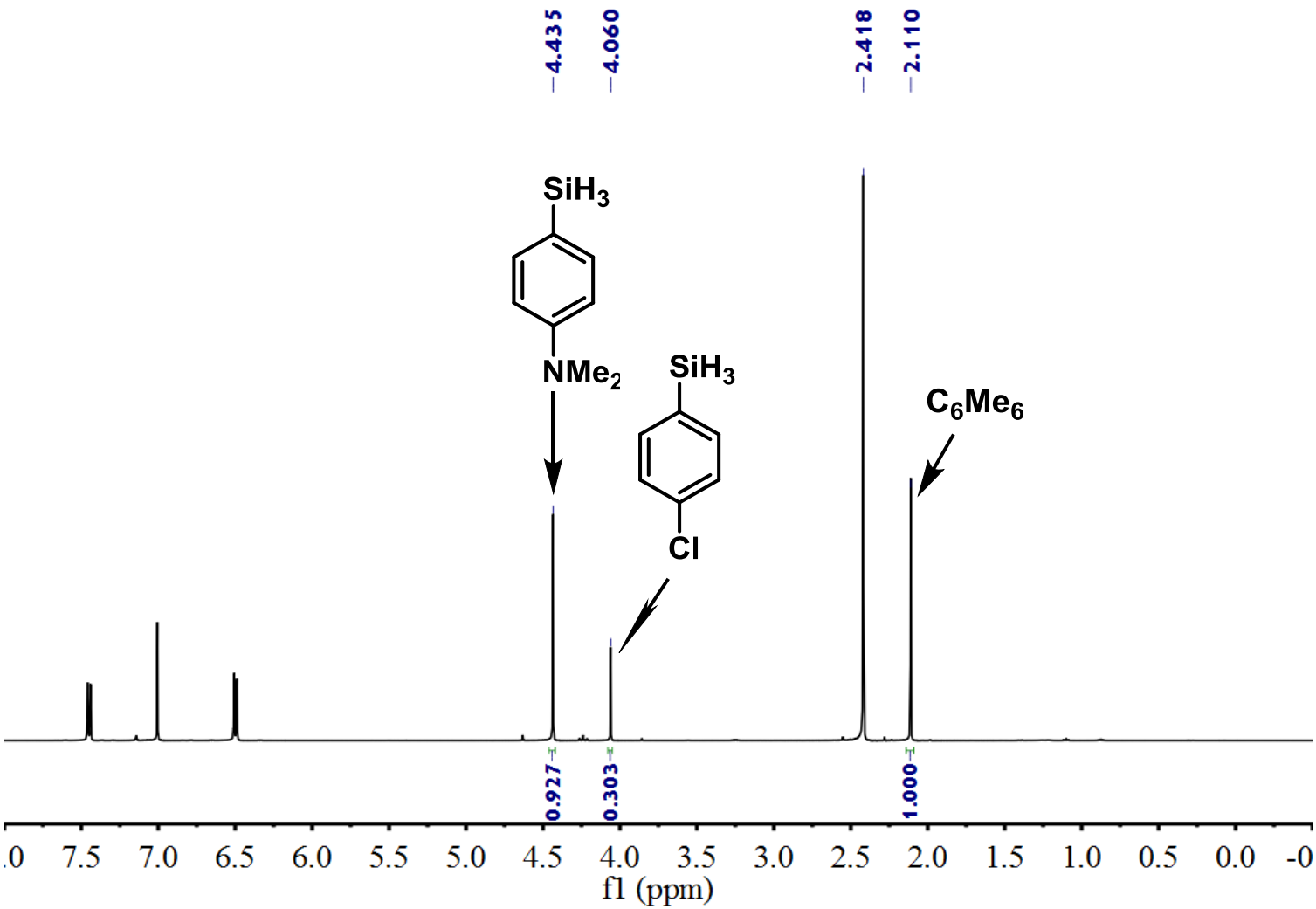

Figure S27. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Cl-$PhSiH_3$ and 4-NMe_2-$PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

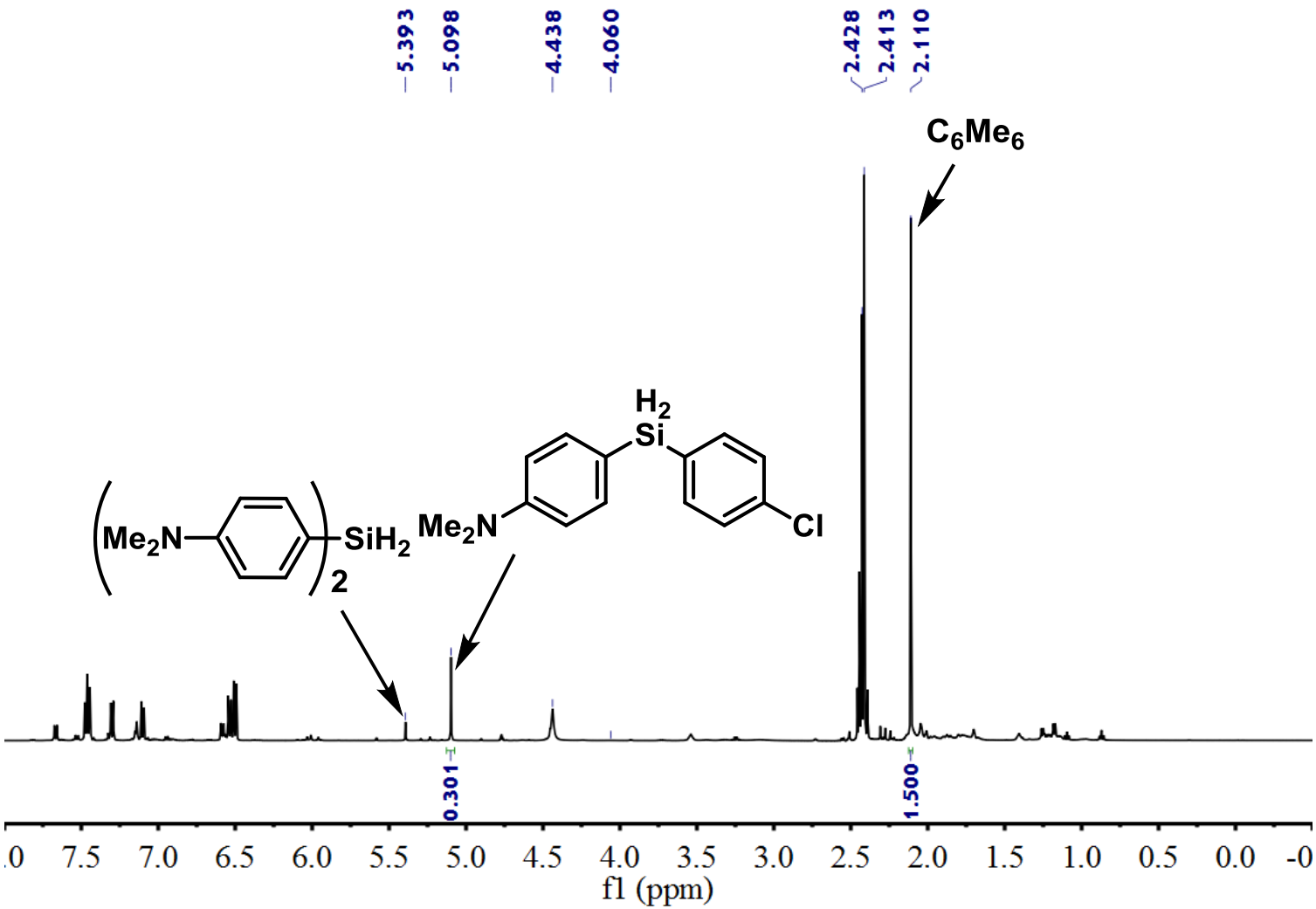

Figure S28. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-Cl-PhSiH$_3$ and 4-NMe$_2$-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

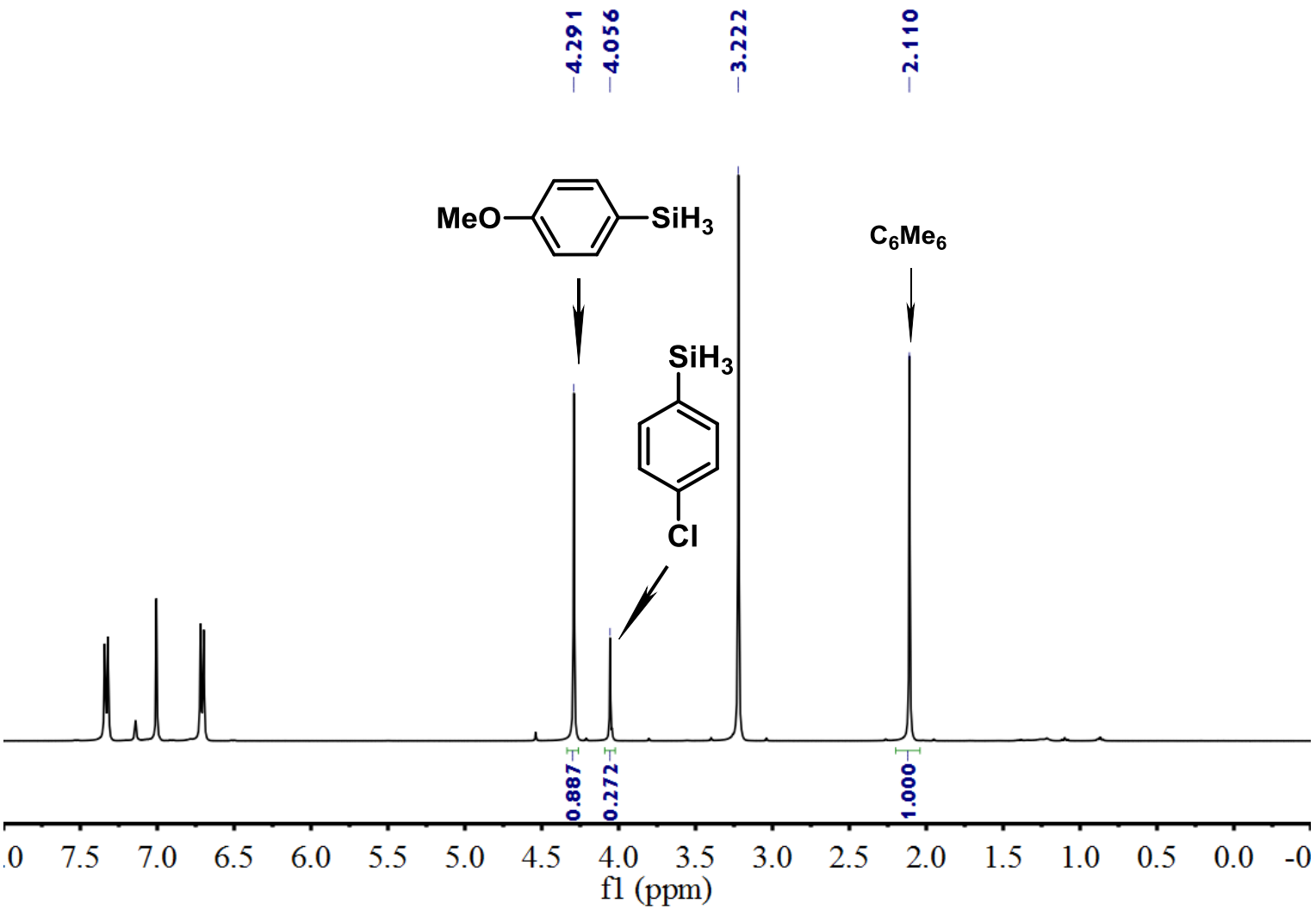

Figure S29. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Cl-PhSiH$_3$ and 4-MeO-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

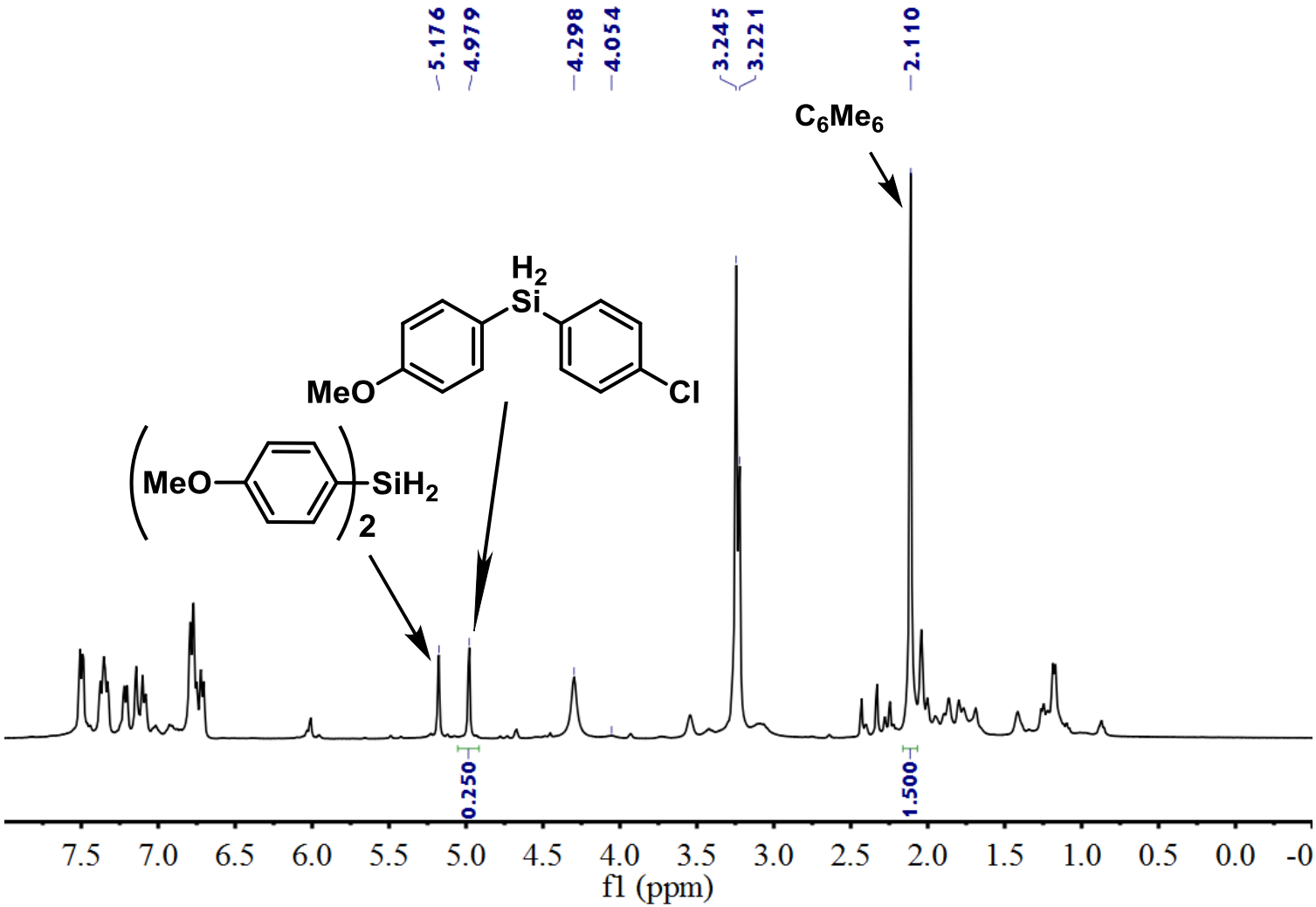

Figure S30. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-Cl-PhSiH$_3$ and 4-MeO-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

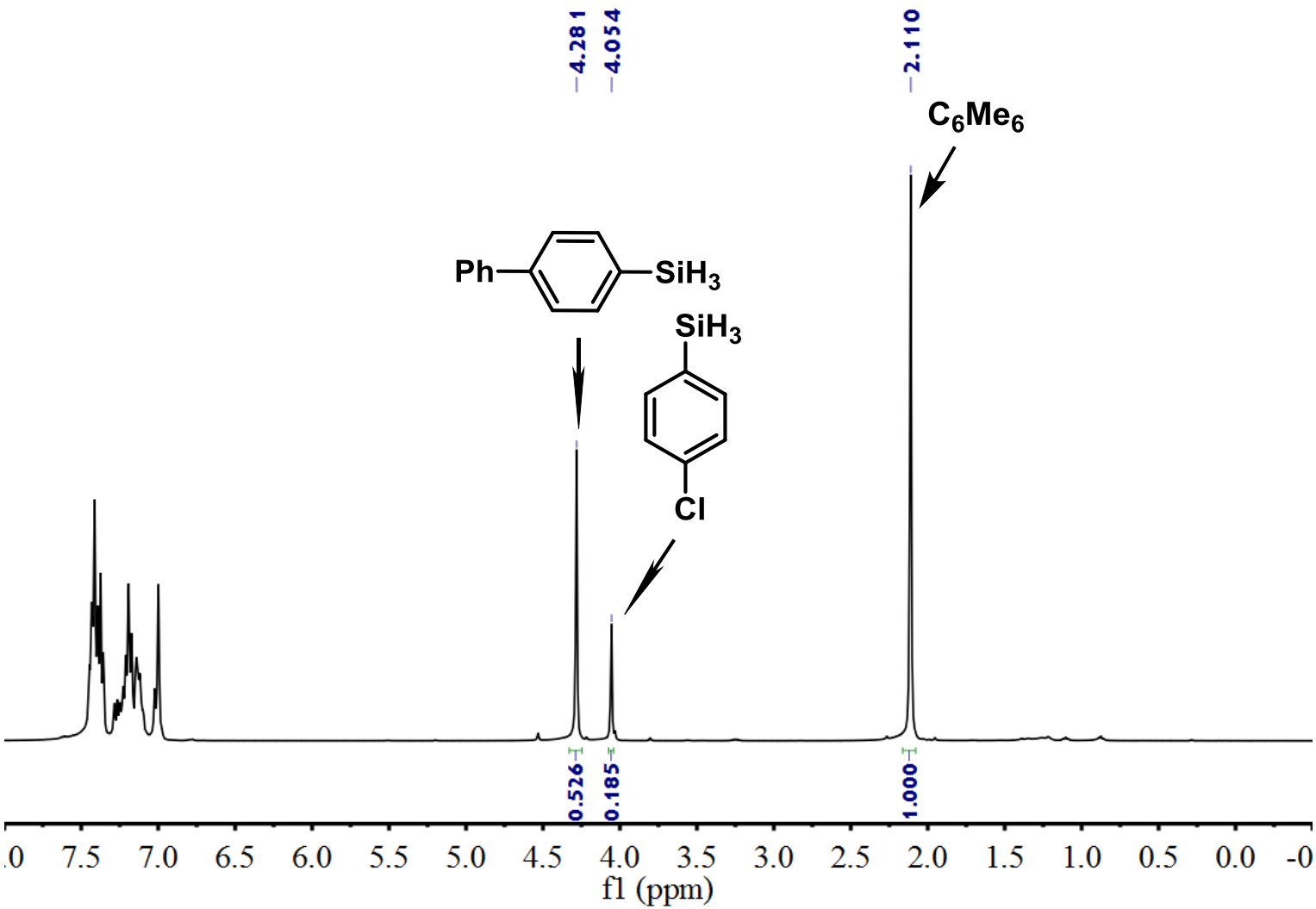

Figure S31. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Cl-PhSiH$_3$ and 4-Ph-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

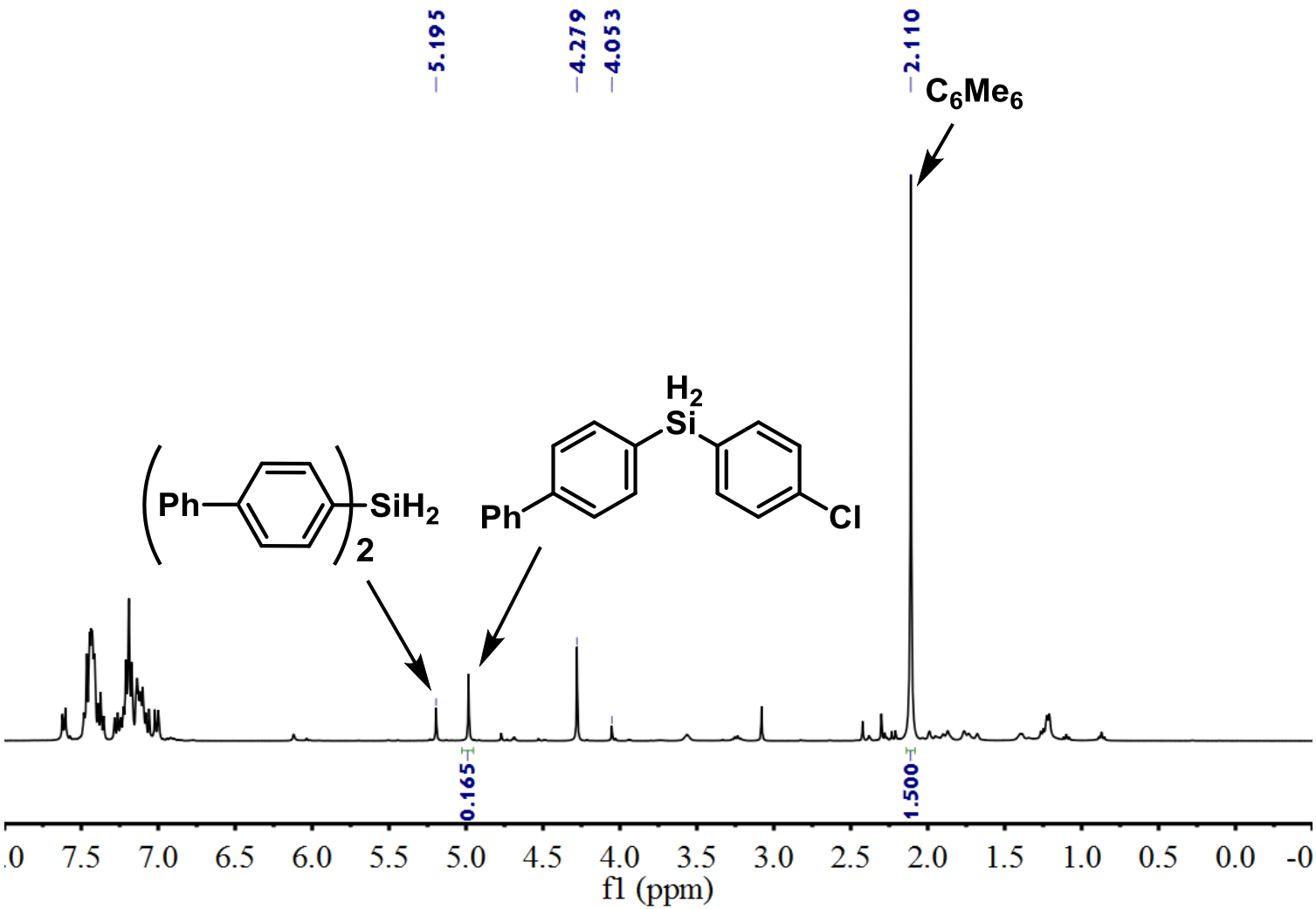

Figure S32. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-Cl-PhSiH$_3$ and 4-Ph-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

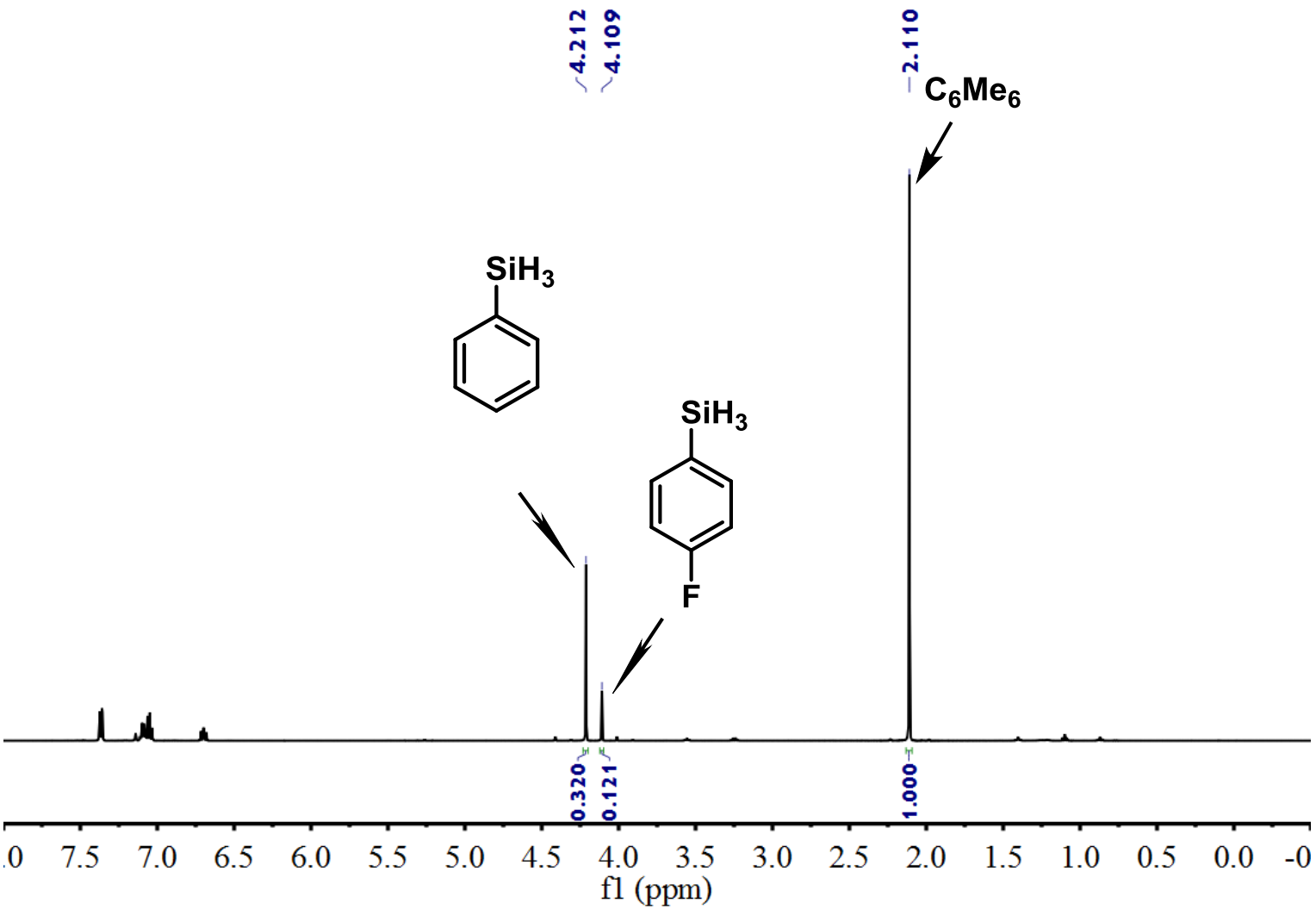

Figure S33. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-F-$PhSiH_3$ and $PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

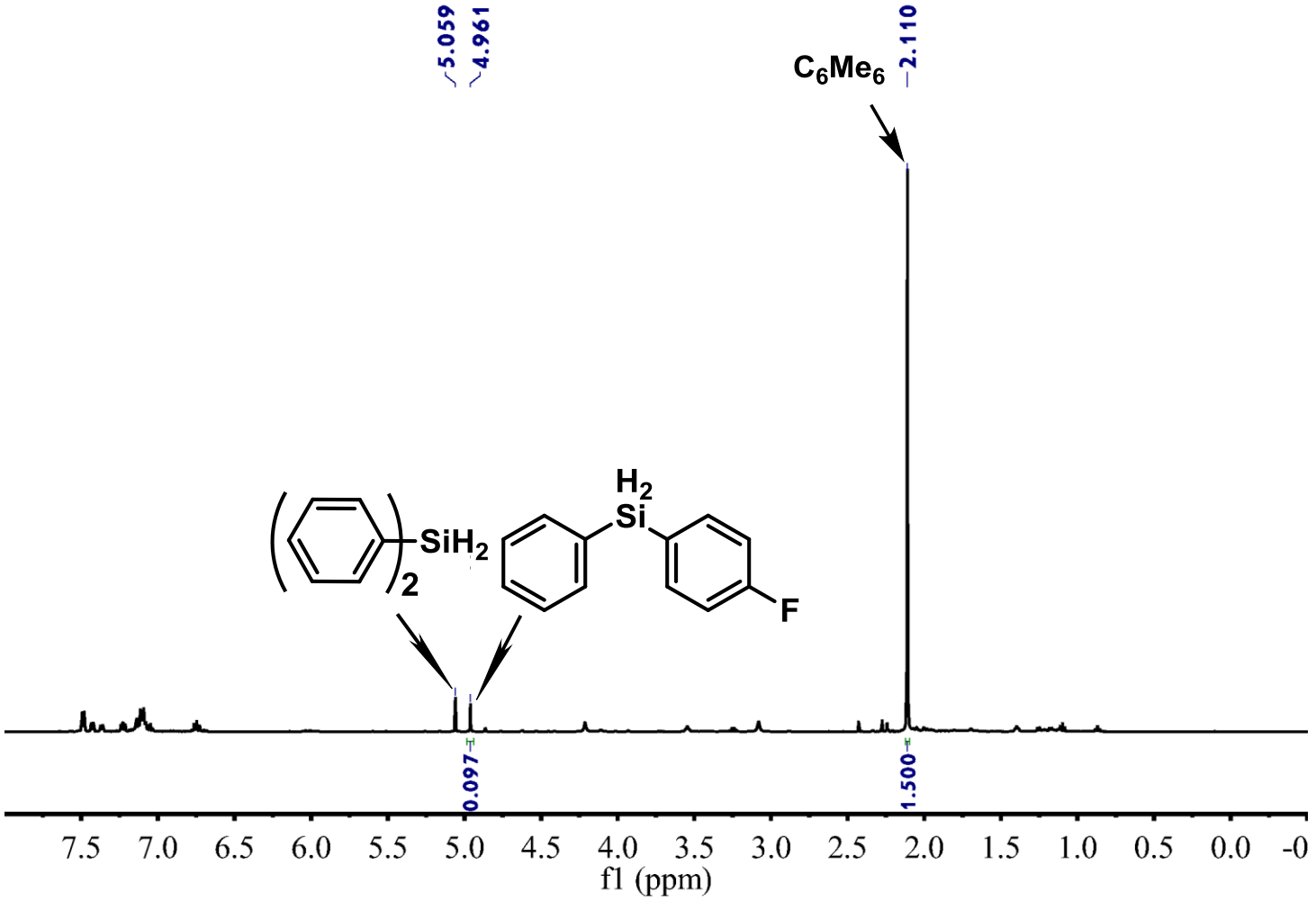

Figure S34. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-F-PhSiH$_3$ and PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

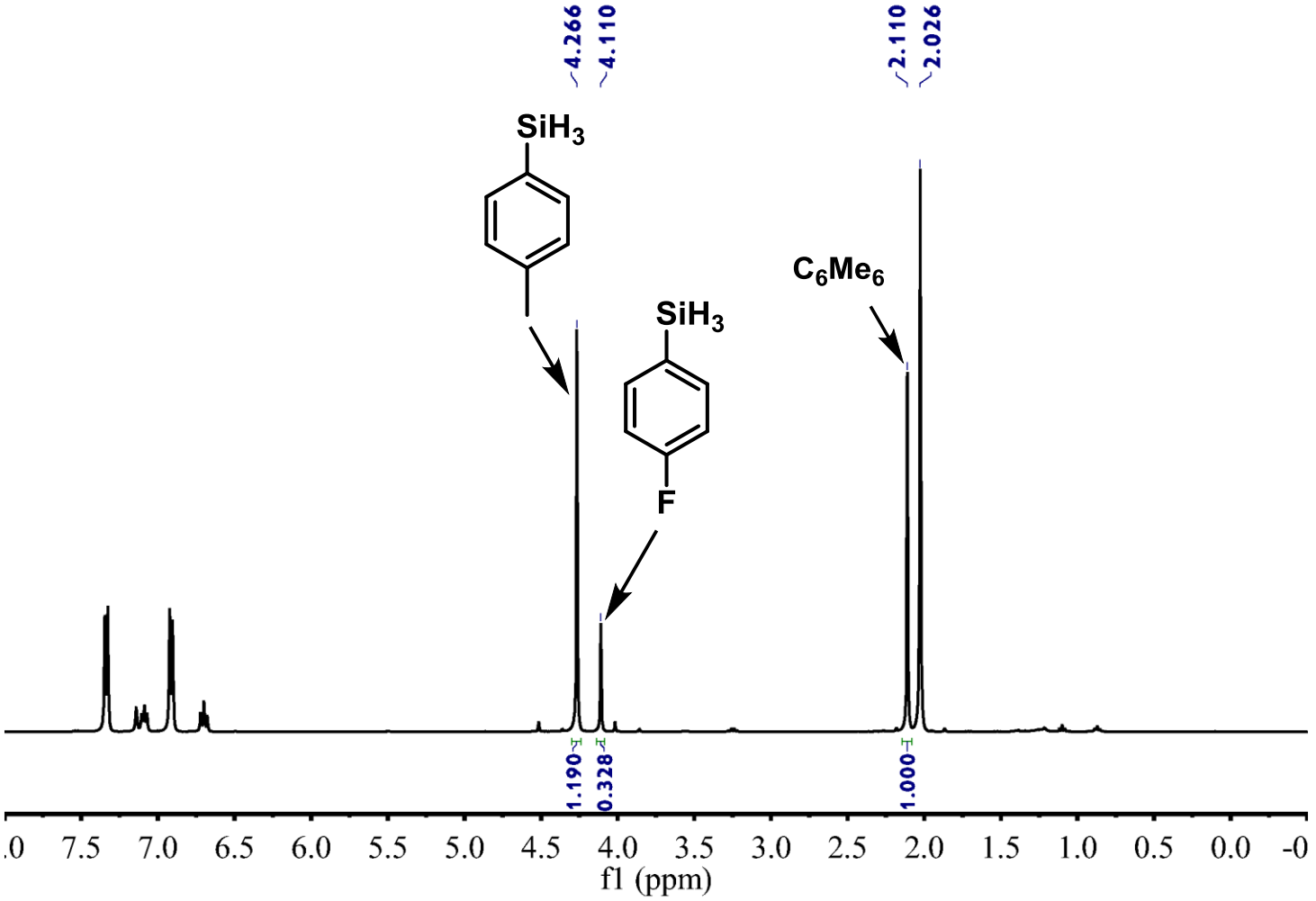

Figure S35. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-F-PhSiH$_3$ and 4-Me-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

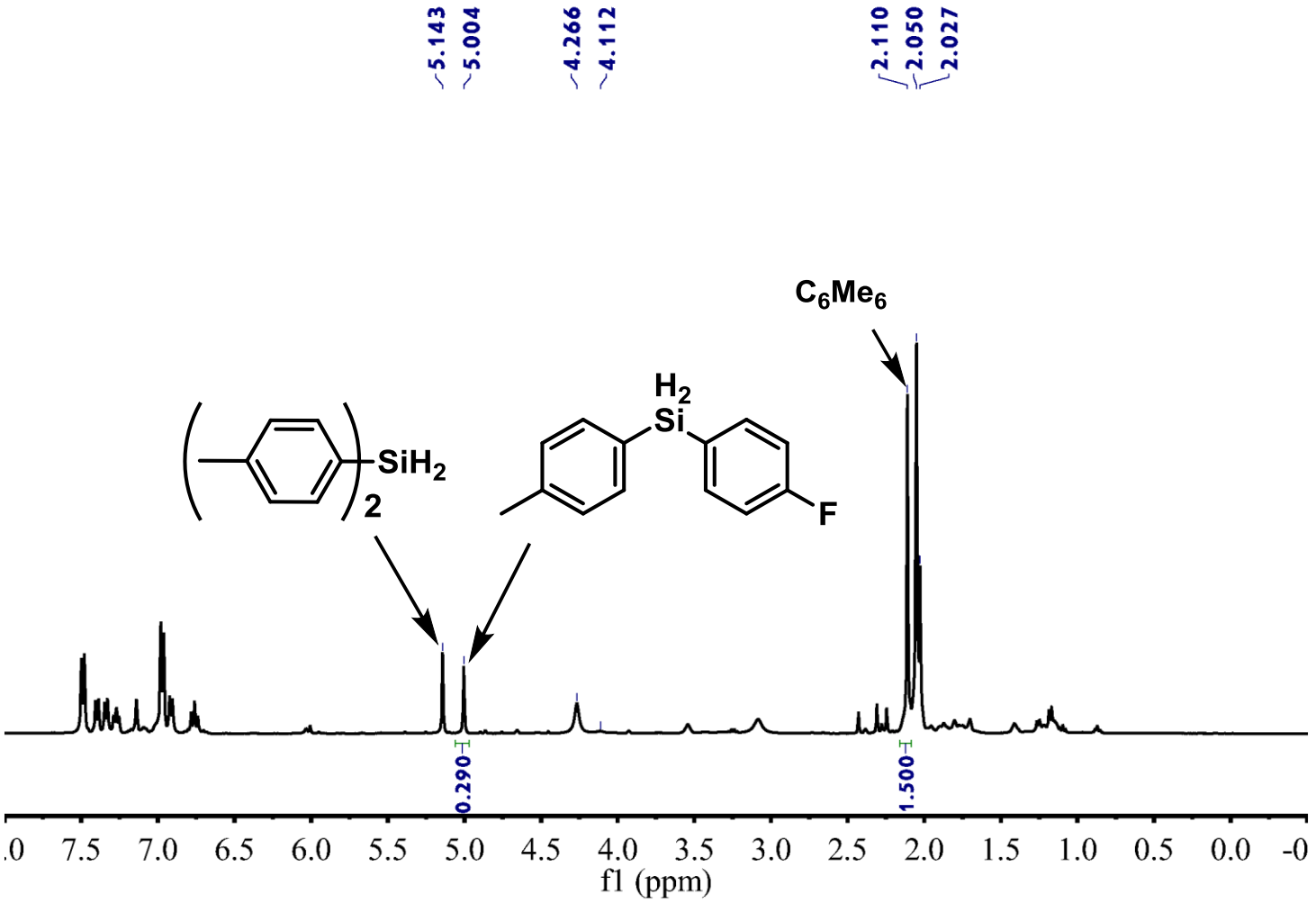

Figure S36. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-F-PhSiH$_3$ and 4-Me-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

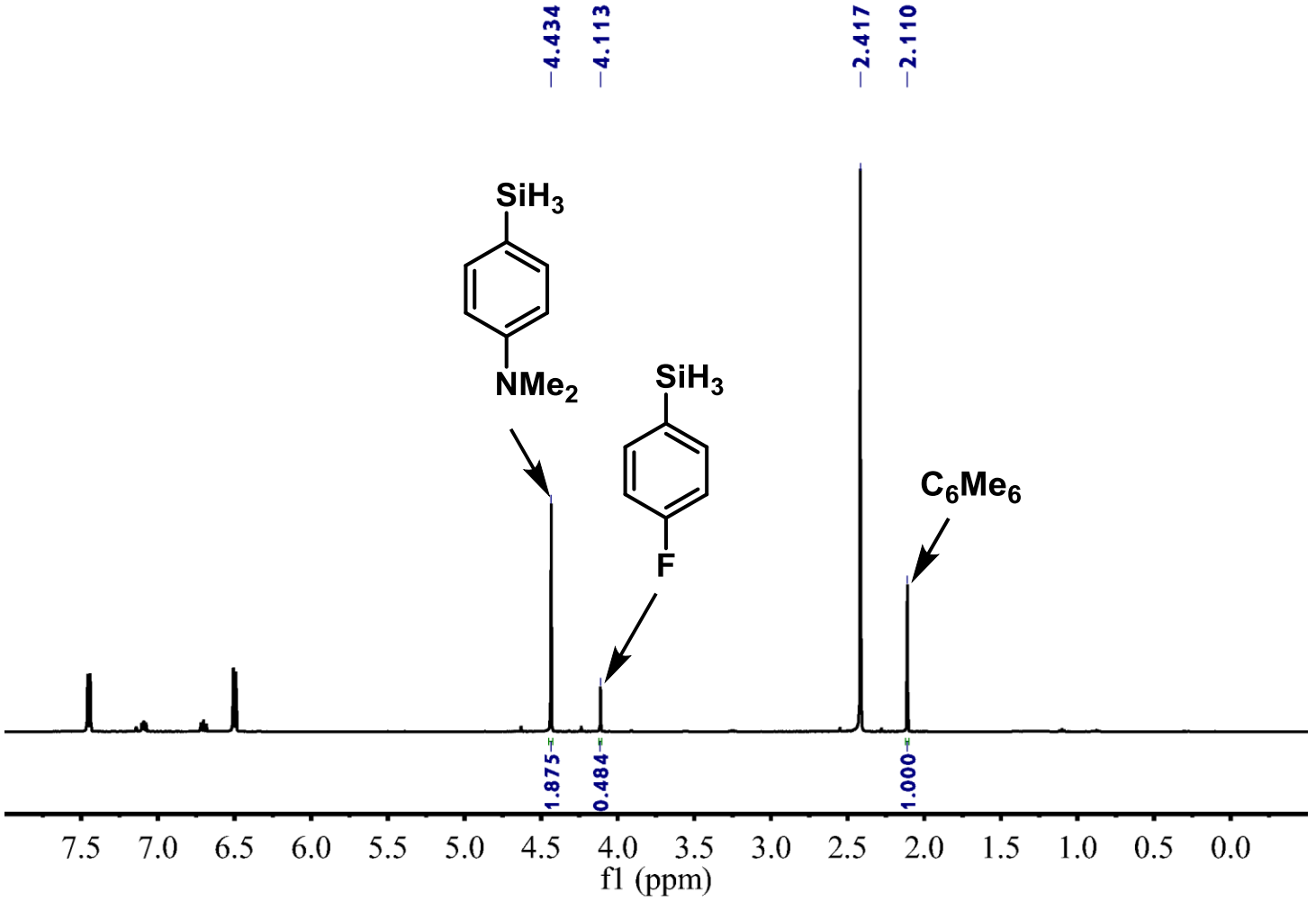

Figure S37. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-F-$PhSiH_3$ and 4-NMe_2-$PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

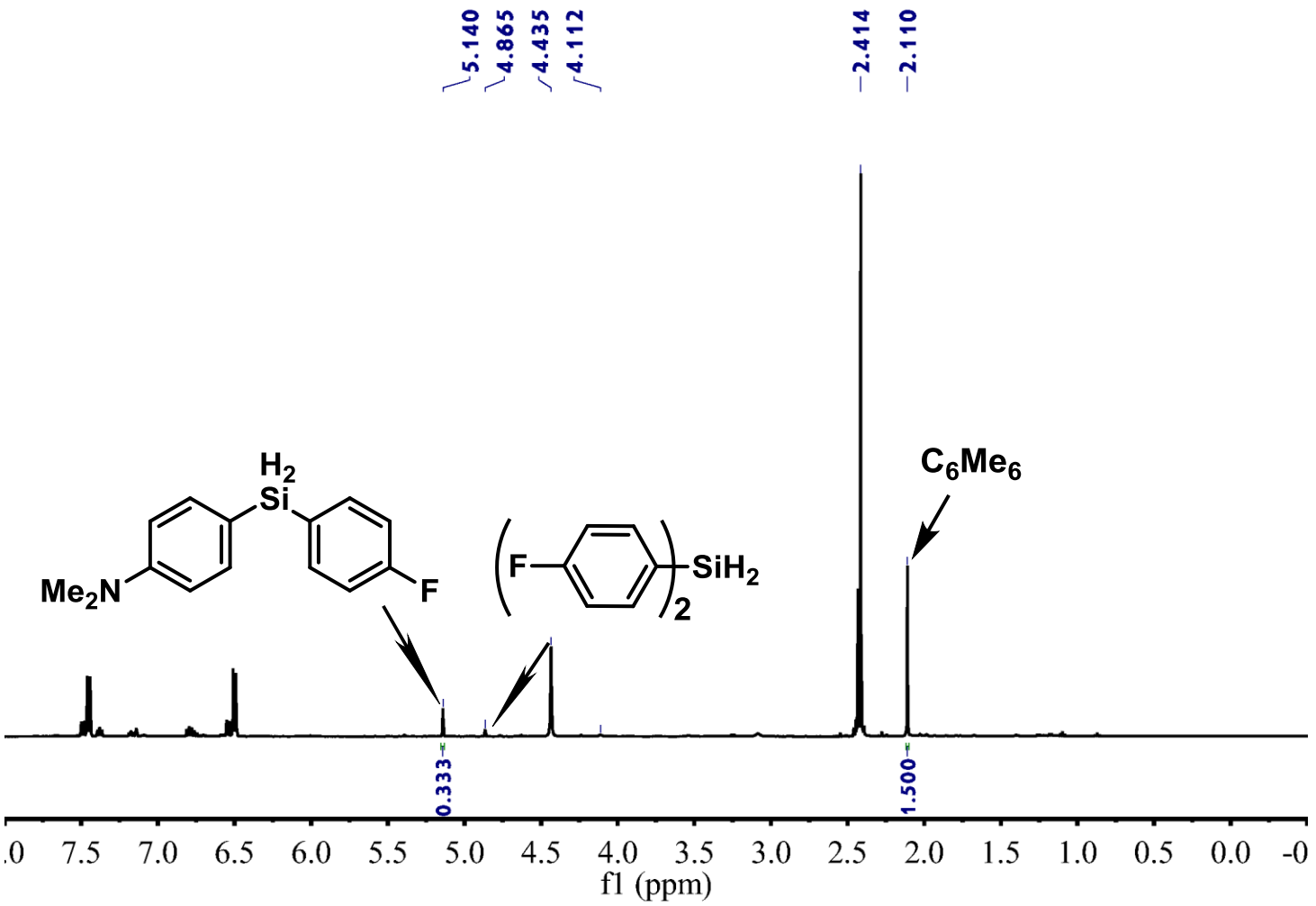

Figure S38. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-F-$PhSiH_3$ and 4-NMe_2-$PhSiH_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

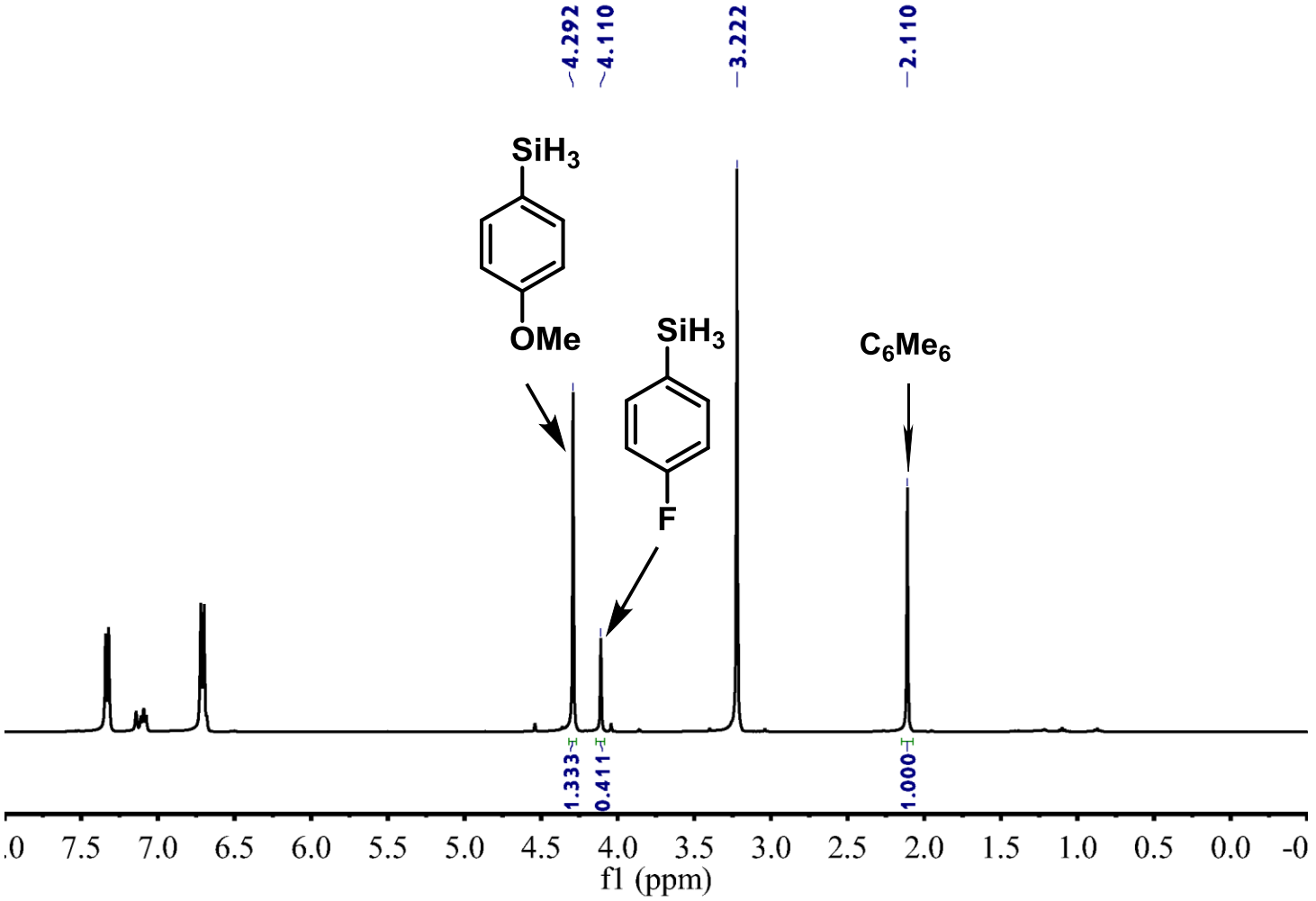

Figure S39. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-F-PhSiH$_3$ and 4-MeO-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

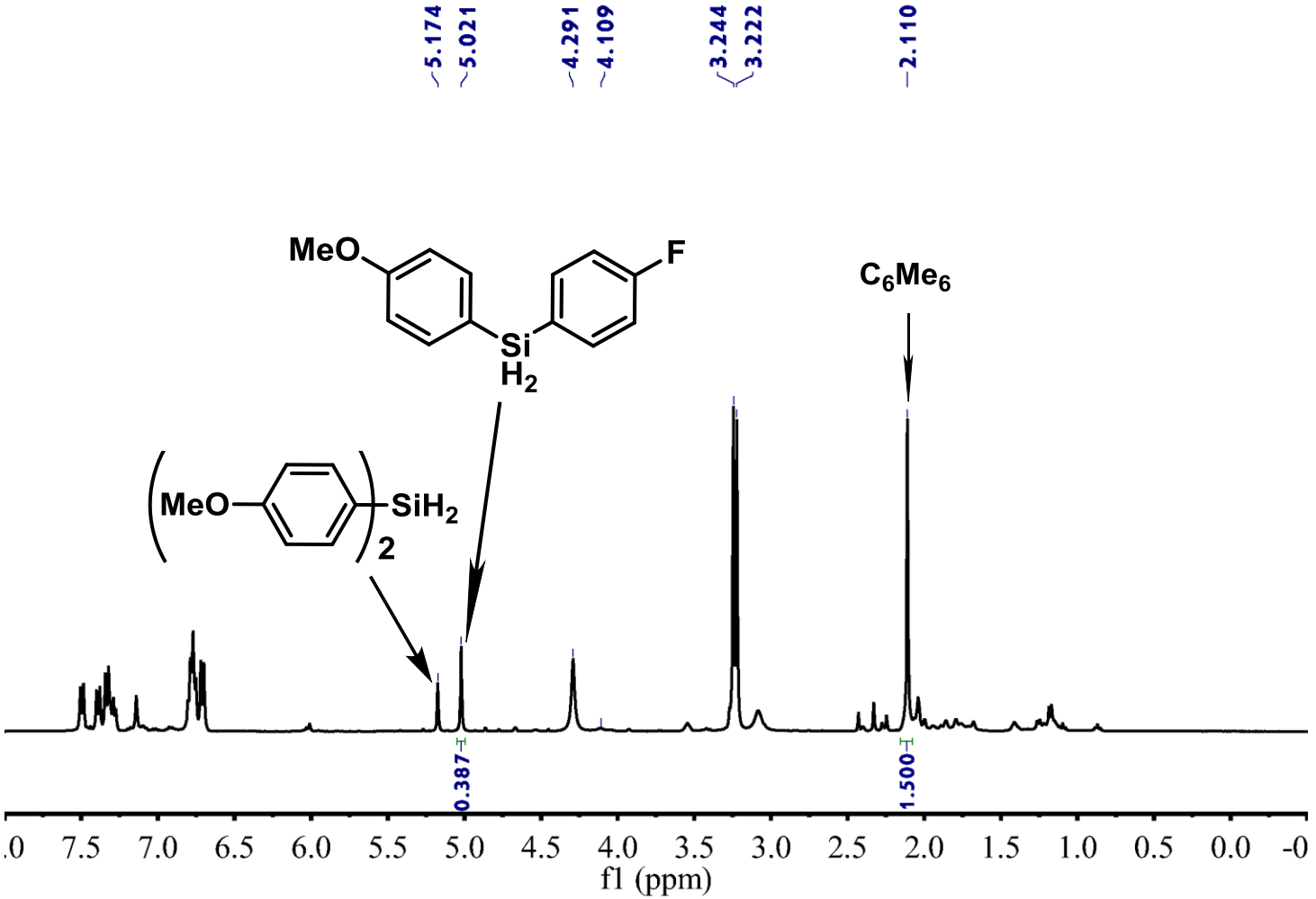

Figure S40. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-F-PhSiH$_3$ and 4-MeO-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

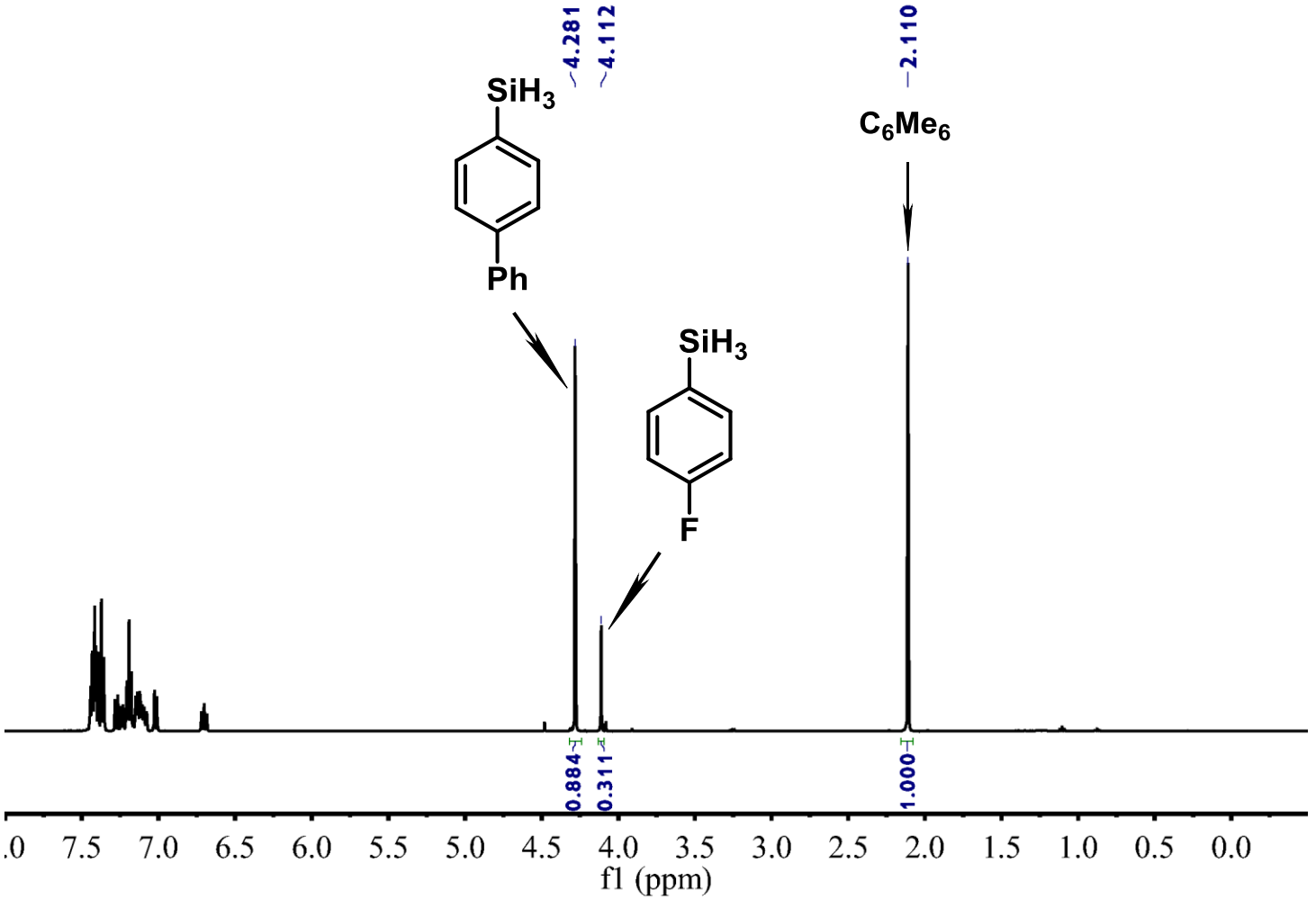

Figure S41. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-F-PhSiH$_3$ and 4-Ph-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

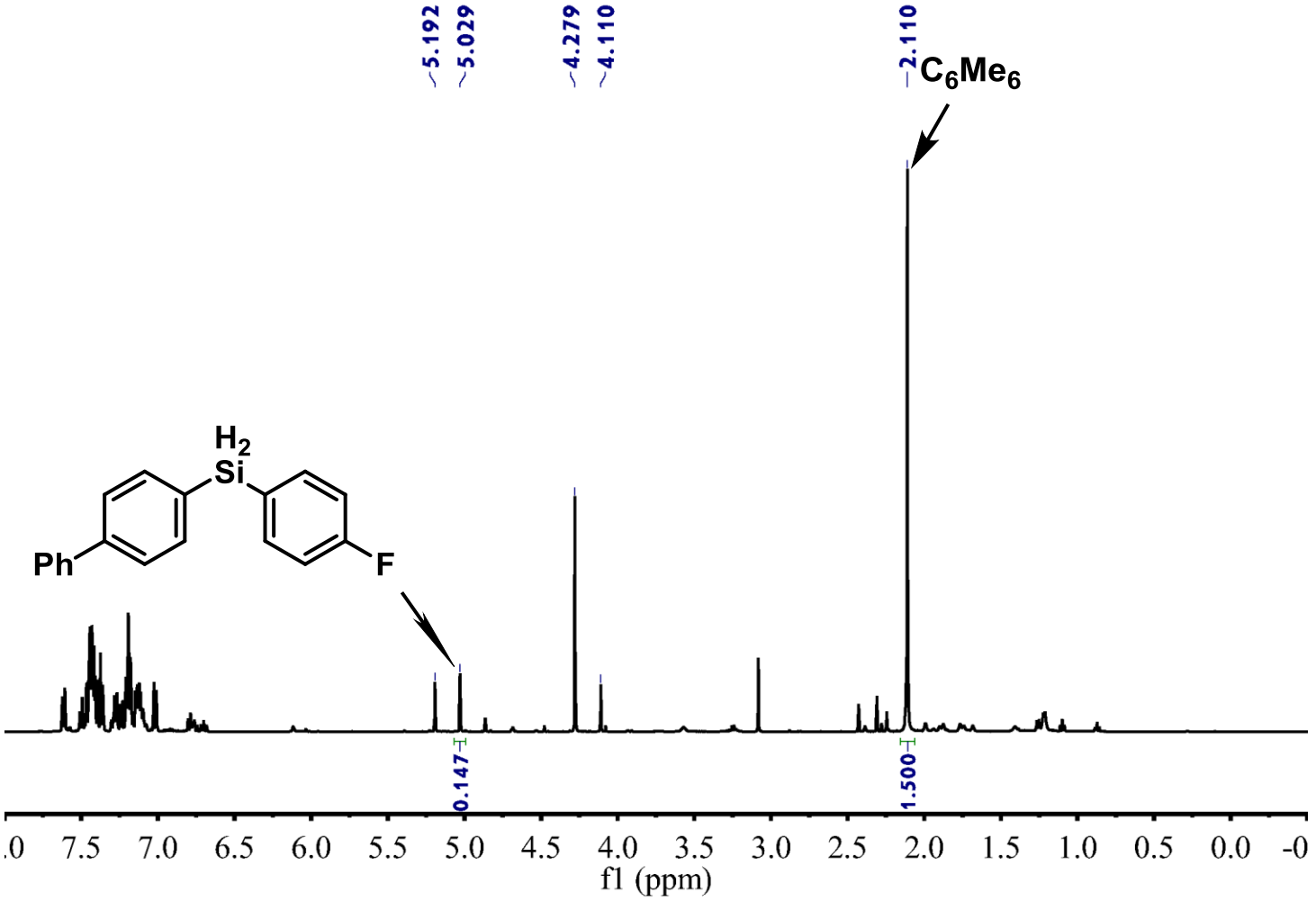

Figure S42. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-F-PhSiH$_3$ and 4-Ph-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 5 min (Table 2) (500 MHz, C_6D_6, 25 ^{o}C).

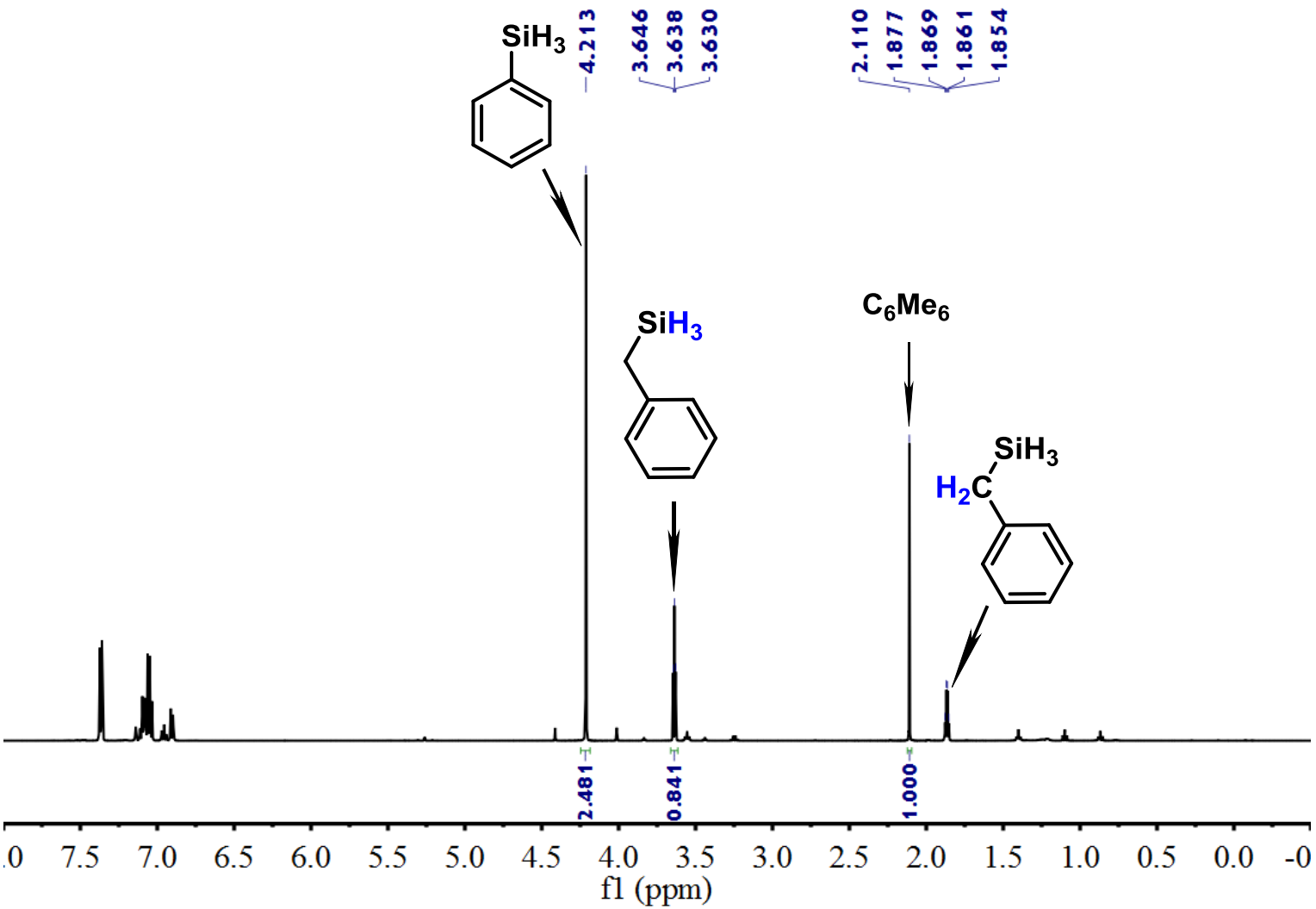

Figure S43. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and $PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

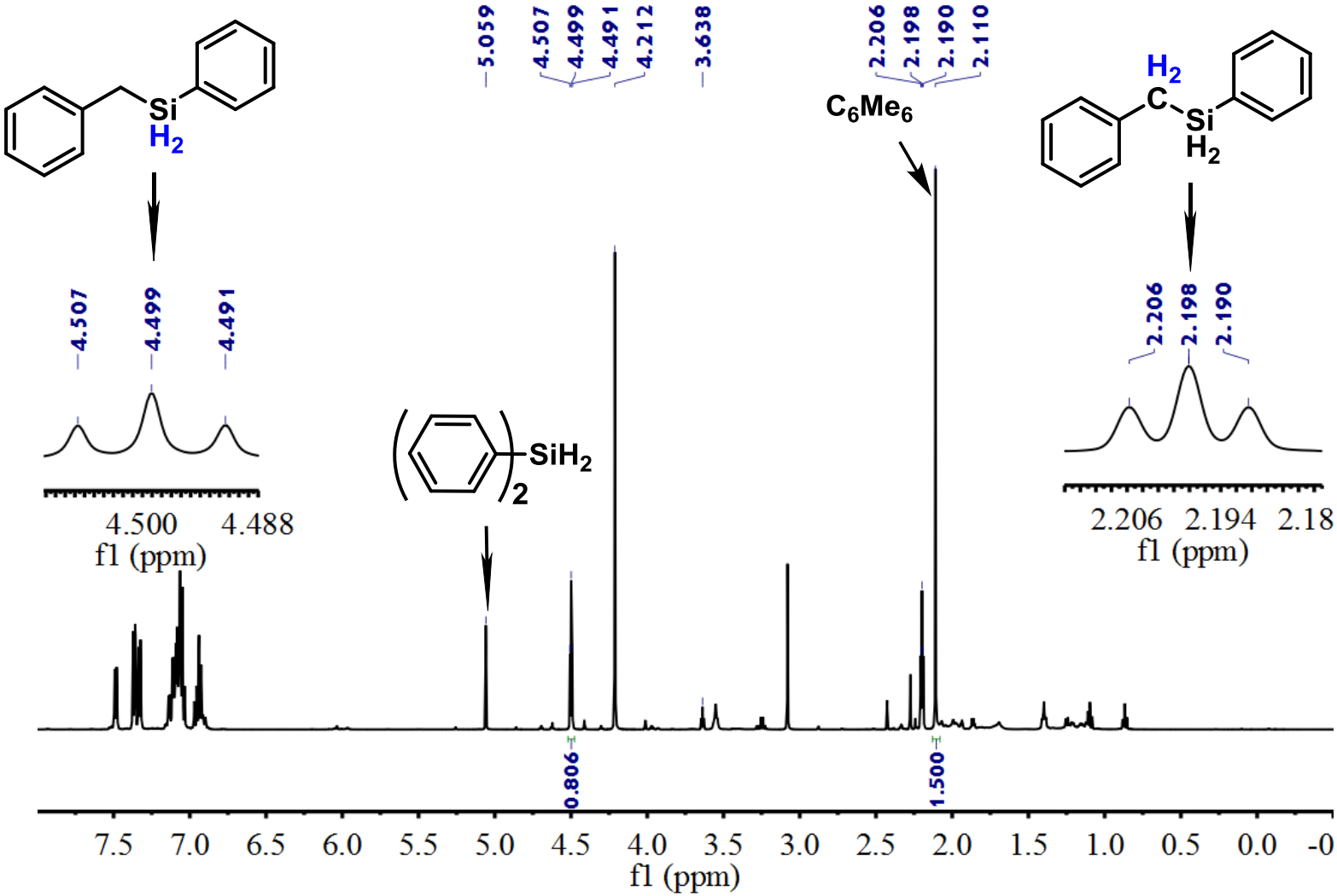

Figure S44. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and $PhSiH_3$ (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

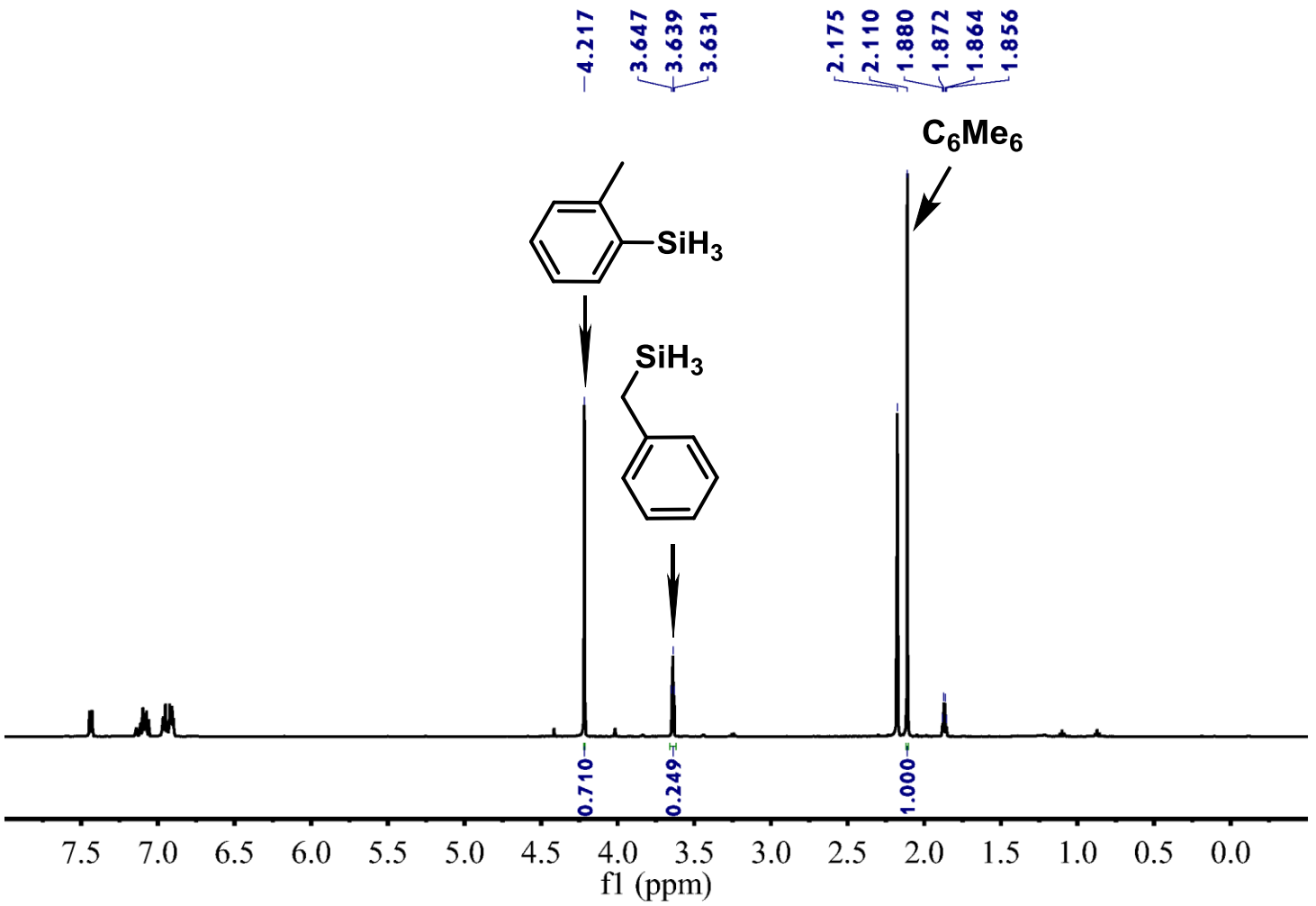

Figure S45. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and 2-Me-$PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

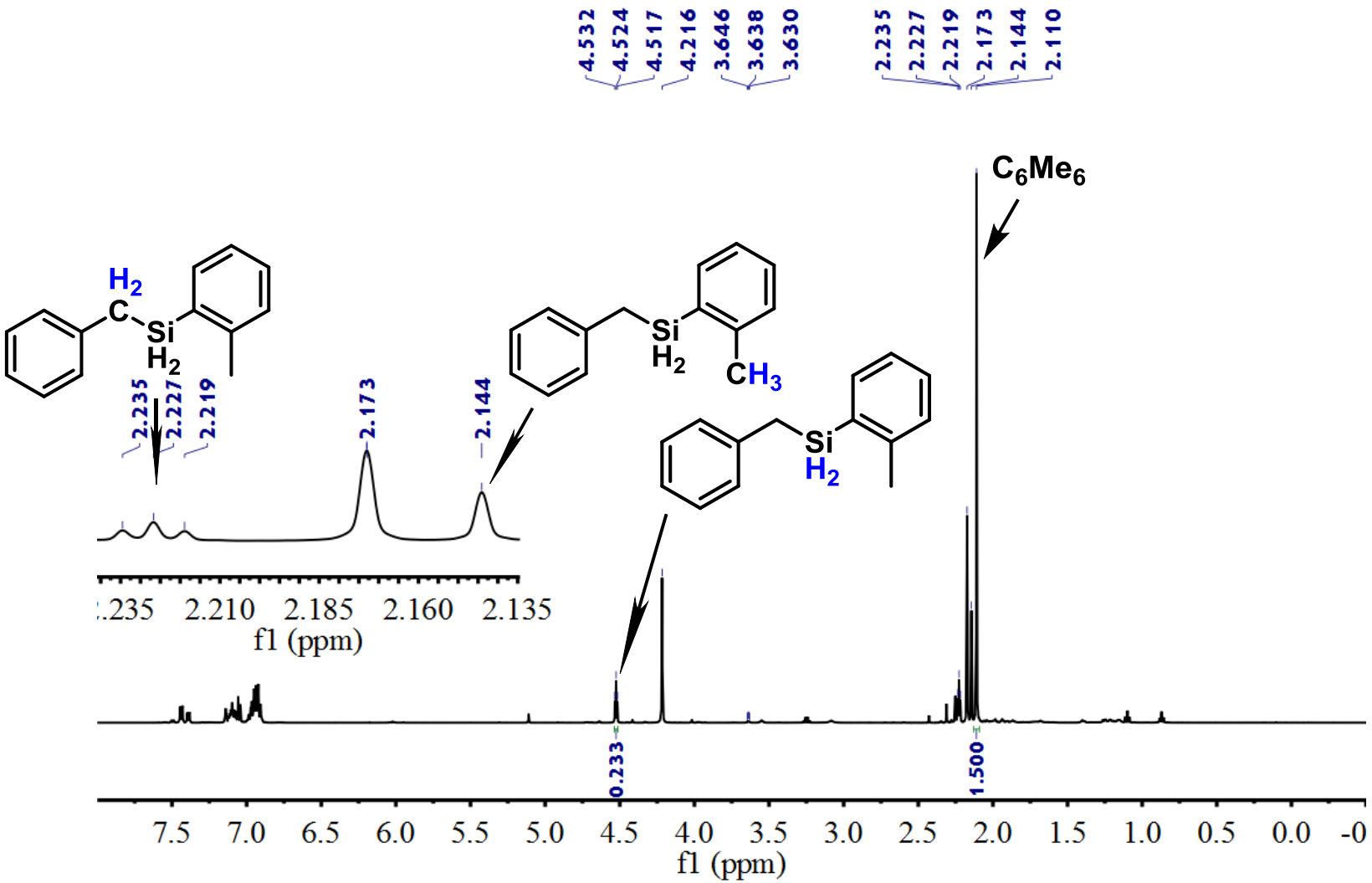

Figure S46. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and 2-Me-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

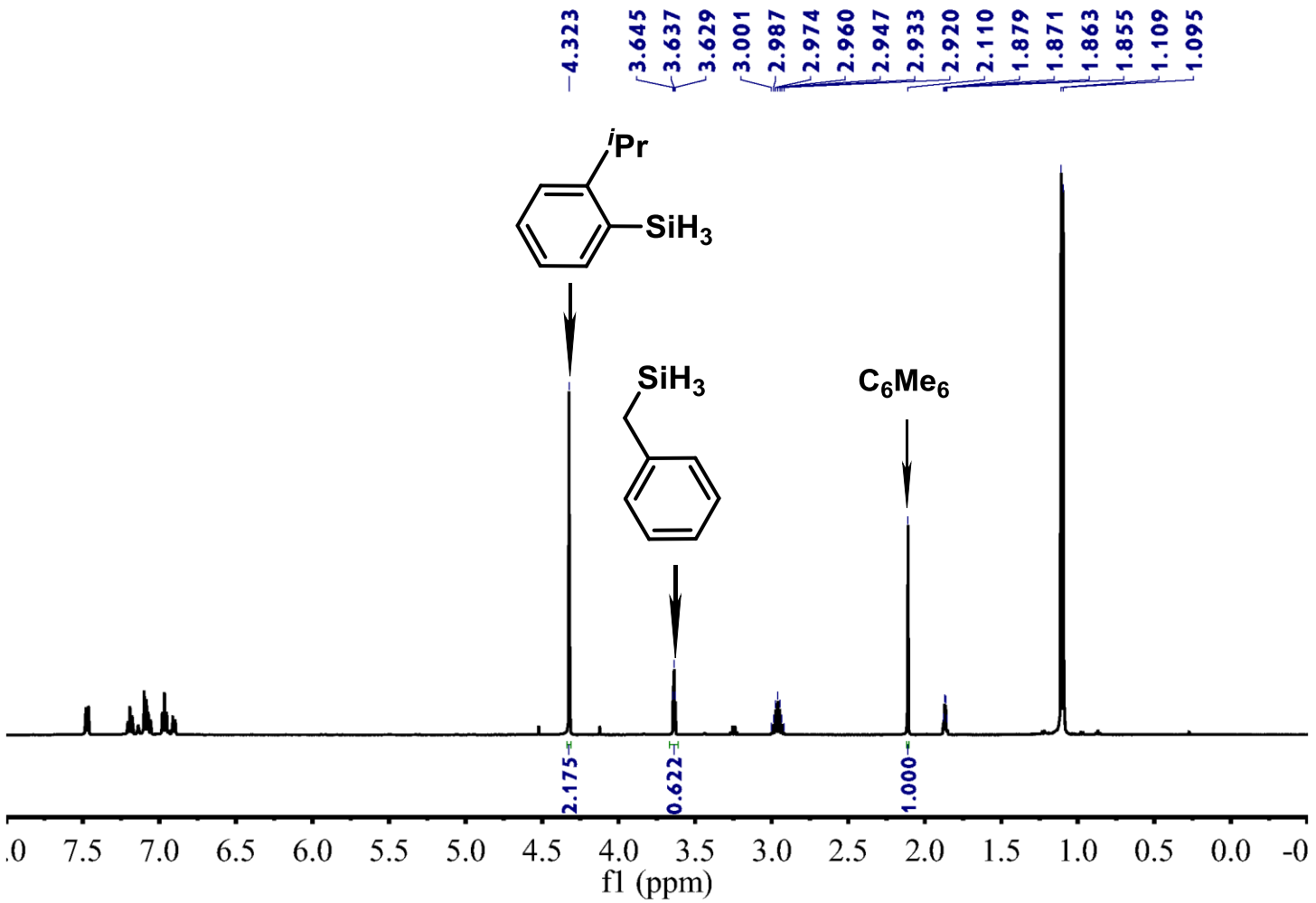

Figure S47. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and 2-^{i}Pr-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

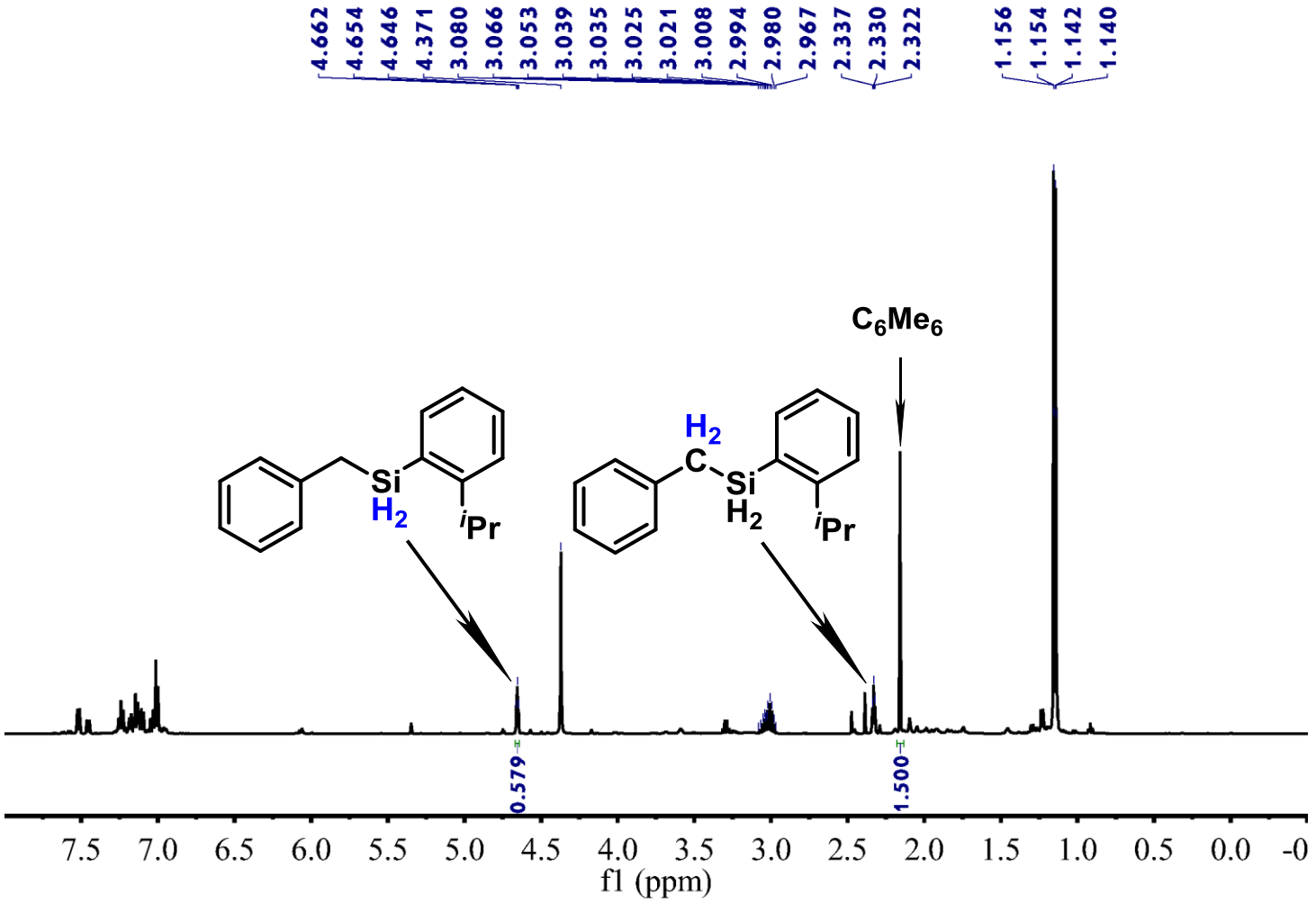

Figure S48. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and 2-^{i}Pr-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

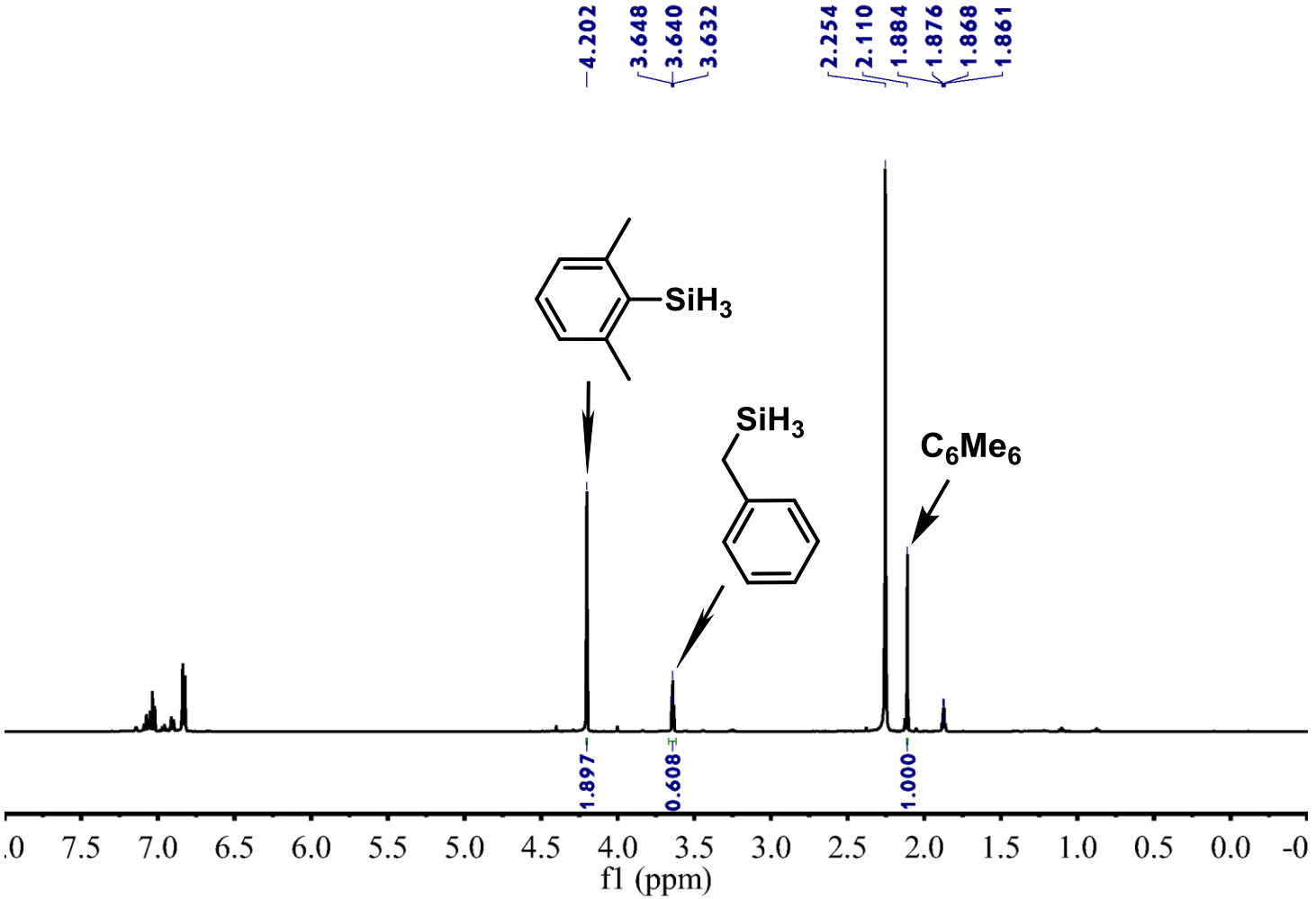

Figure S49. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and 2,6-Me_2-$PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

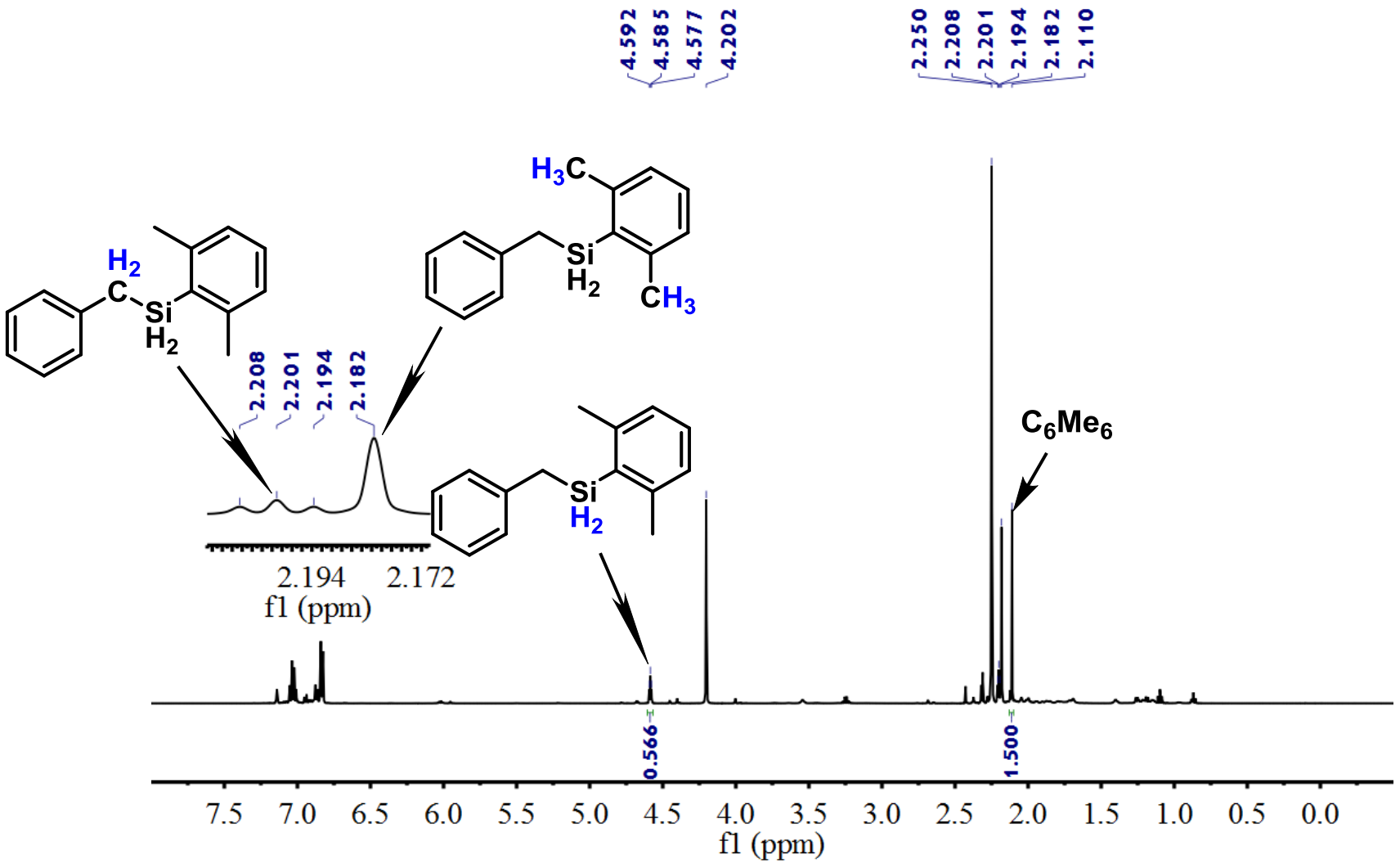

Figure S50. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and 2,6-Me_2-PhSiH_3 (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

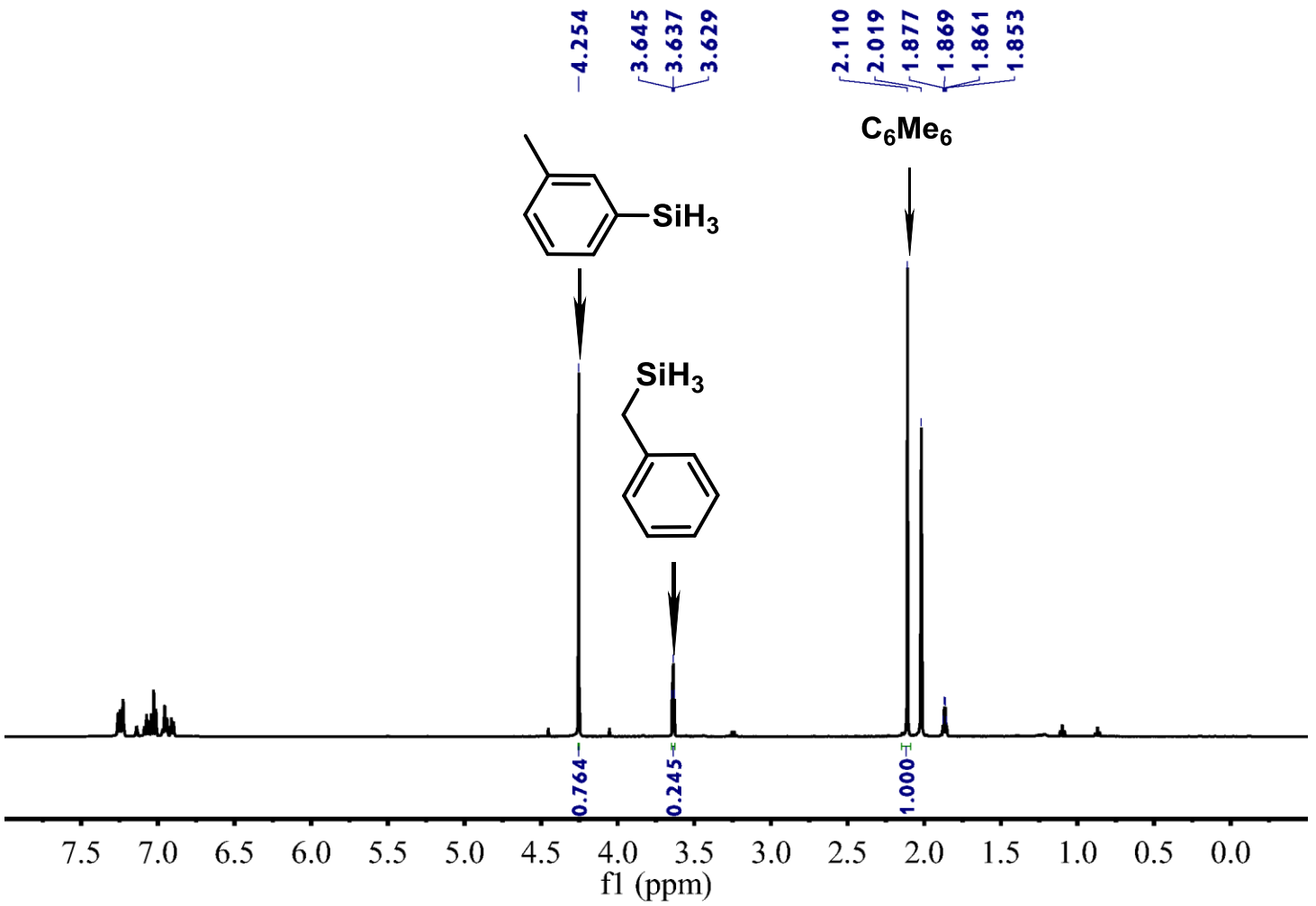

Figure S51. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and 3-Me-PhSiH_3 (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

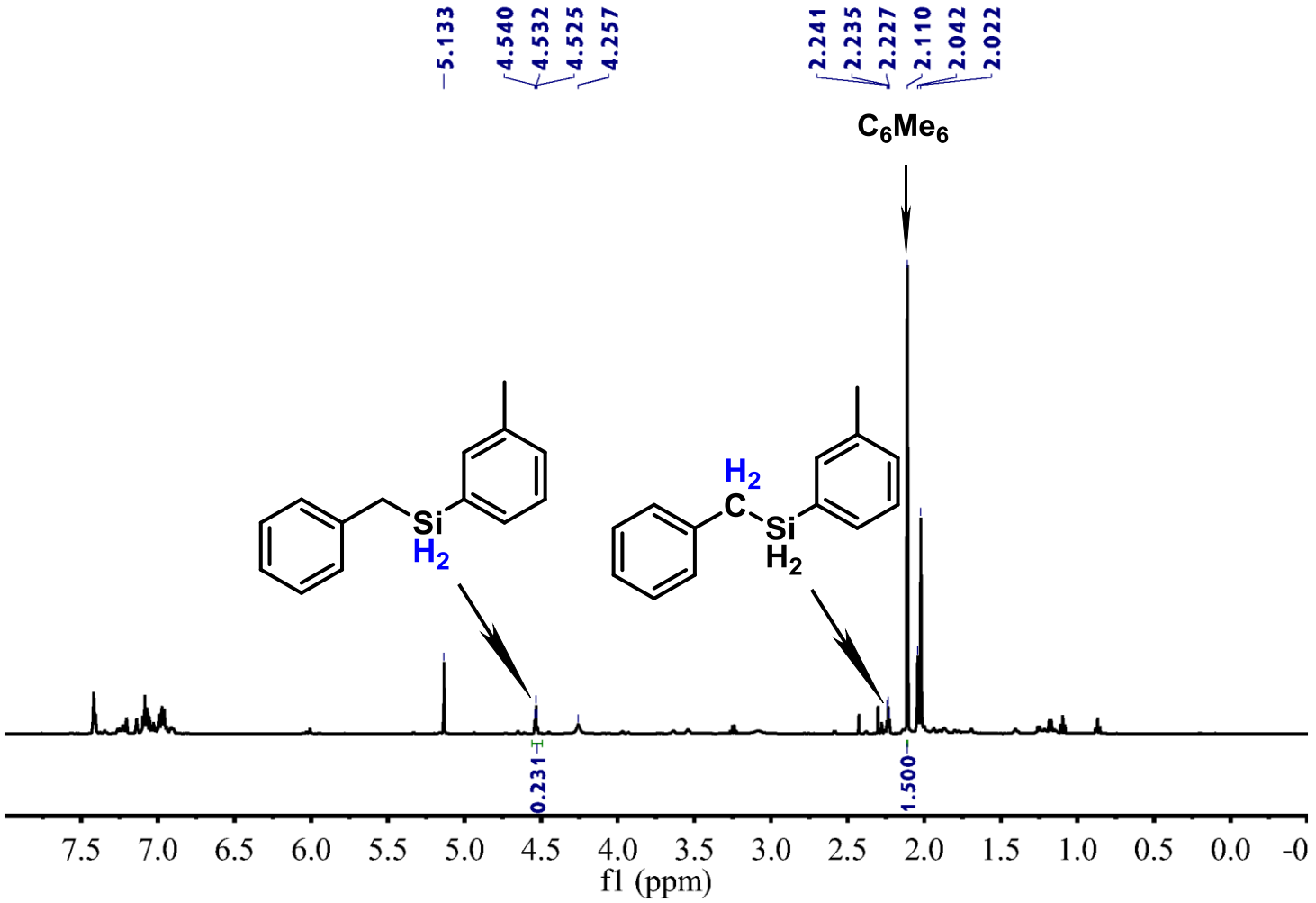

Figure S52. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and 3-Me-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

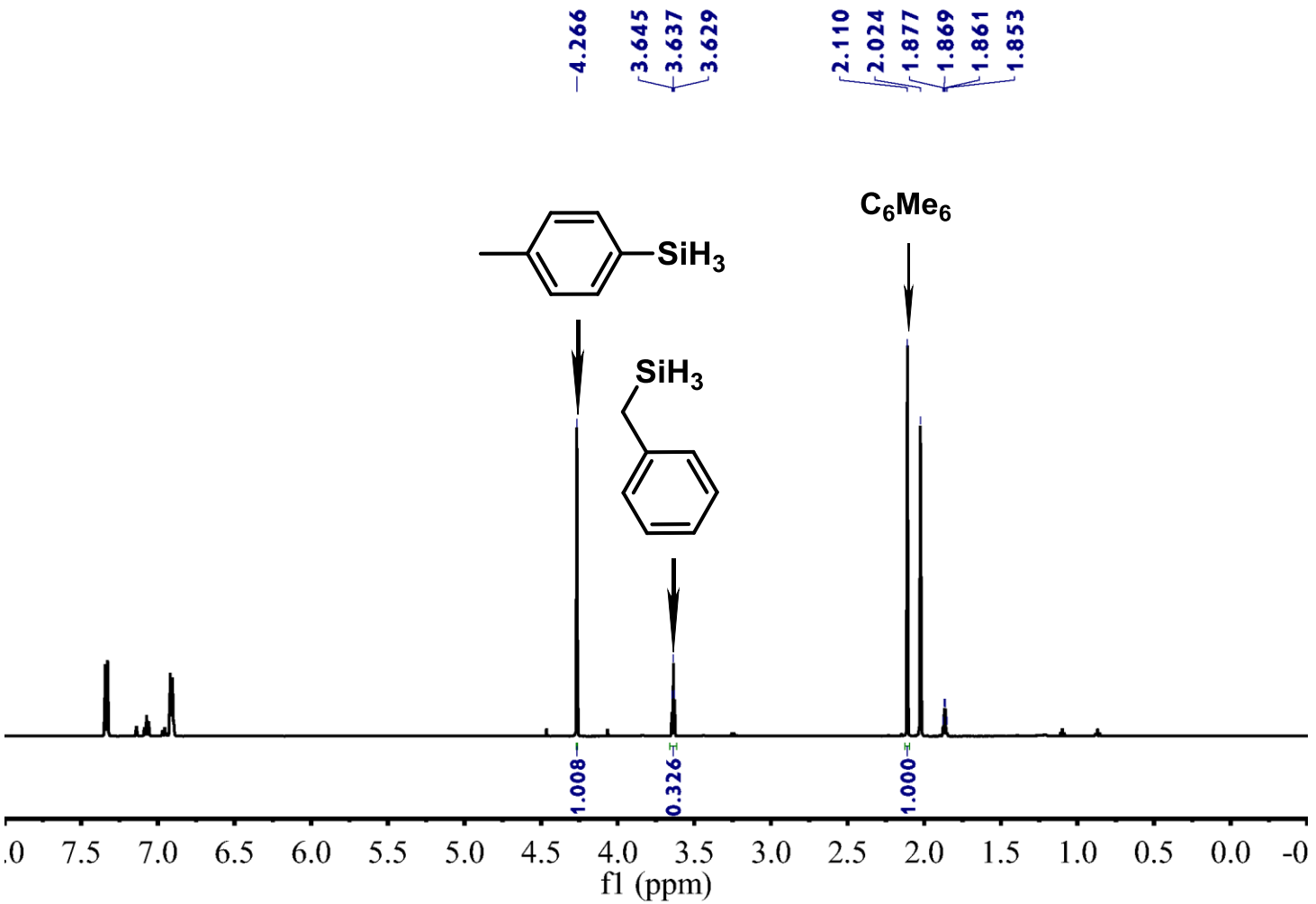

Figure S53. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and 4-Me-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

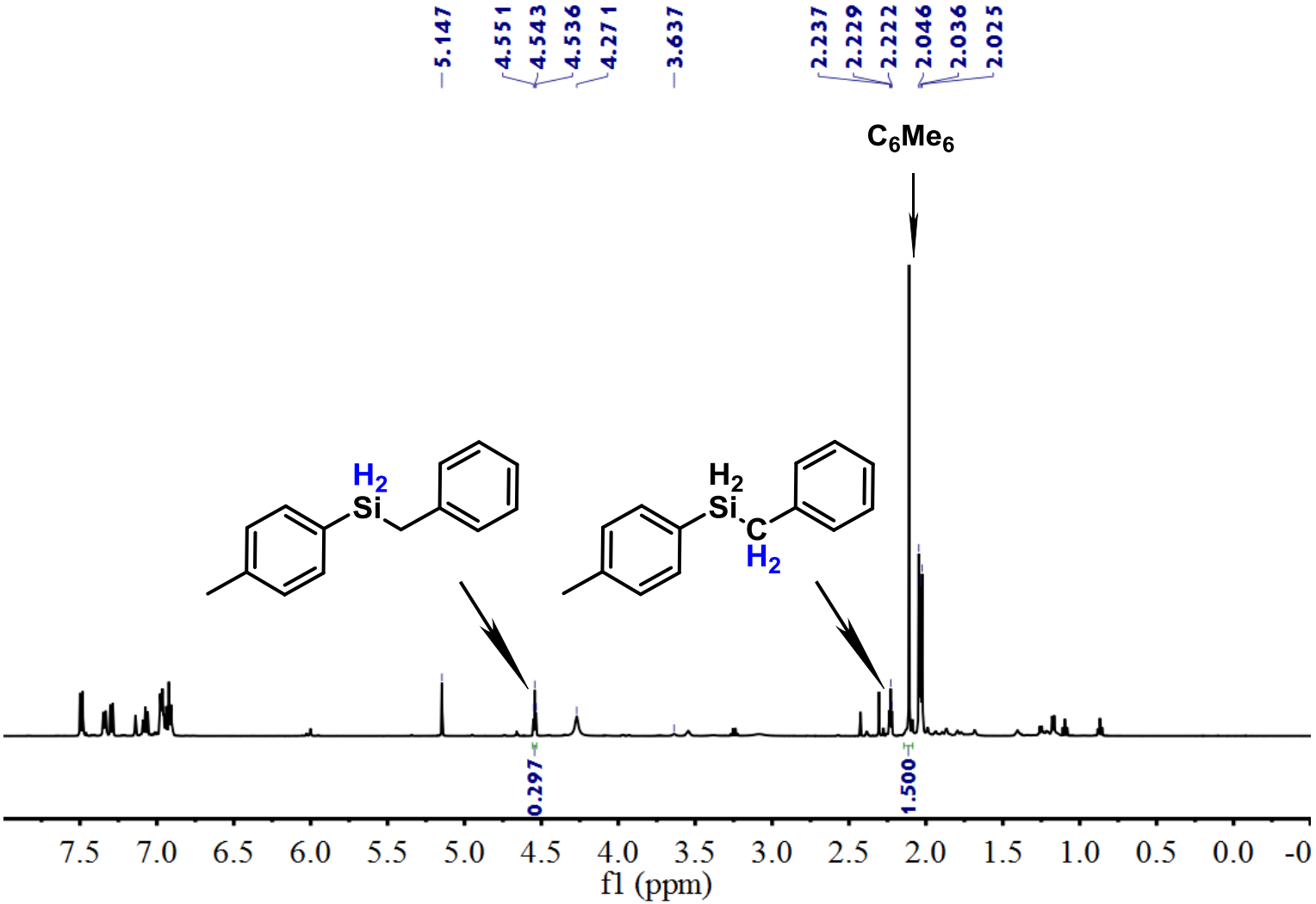

Figure S54. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and 4-Me-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

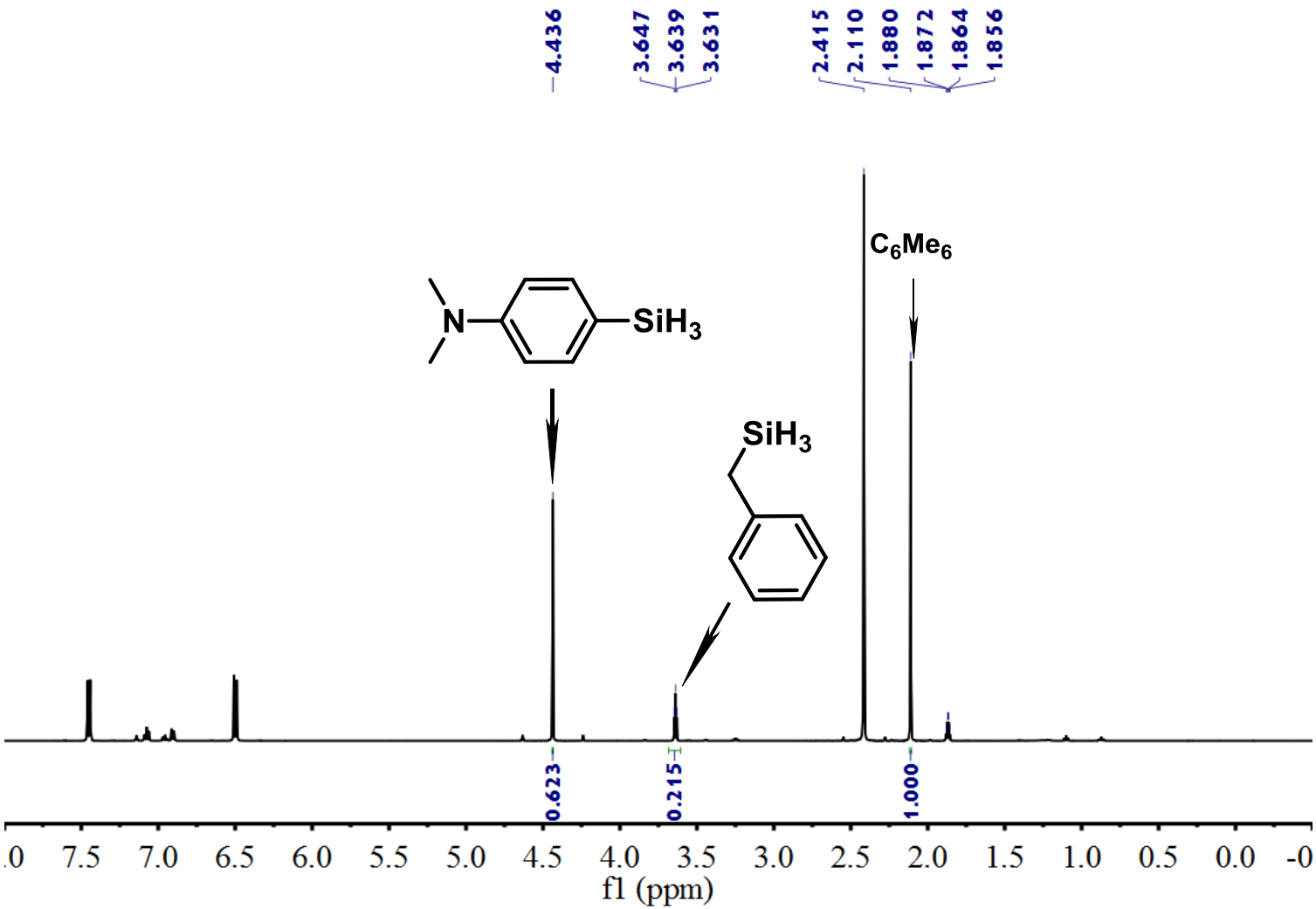

Figure S55. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and 4-NMe_2-$PhSiH_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

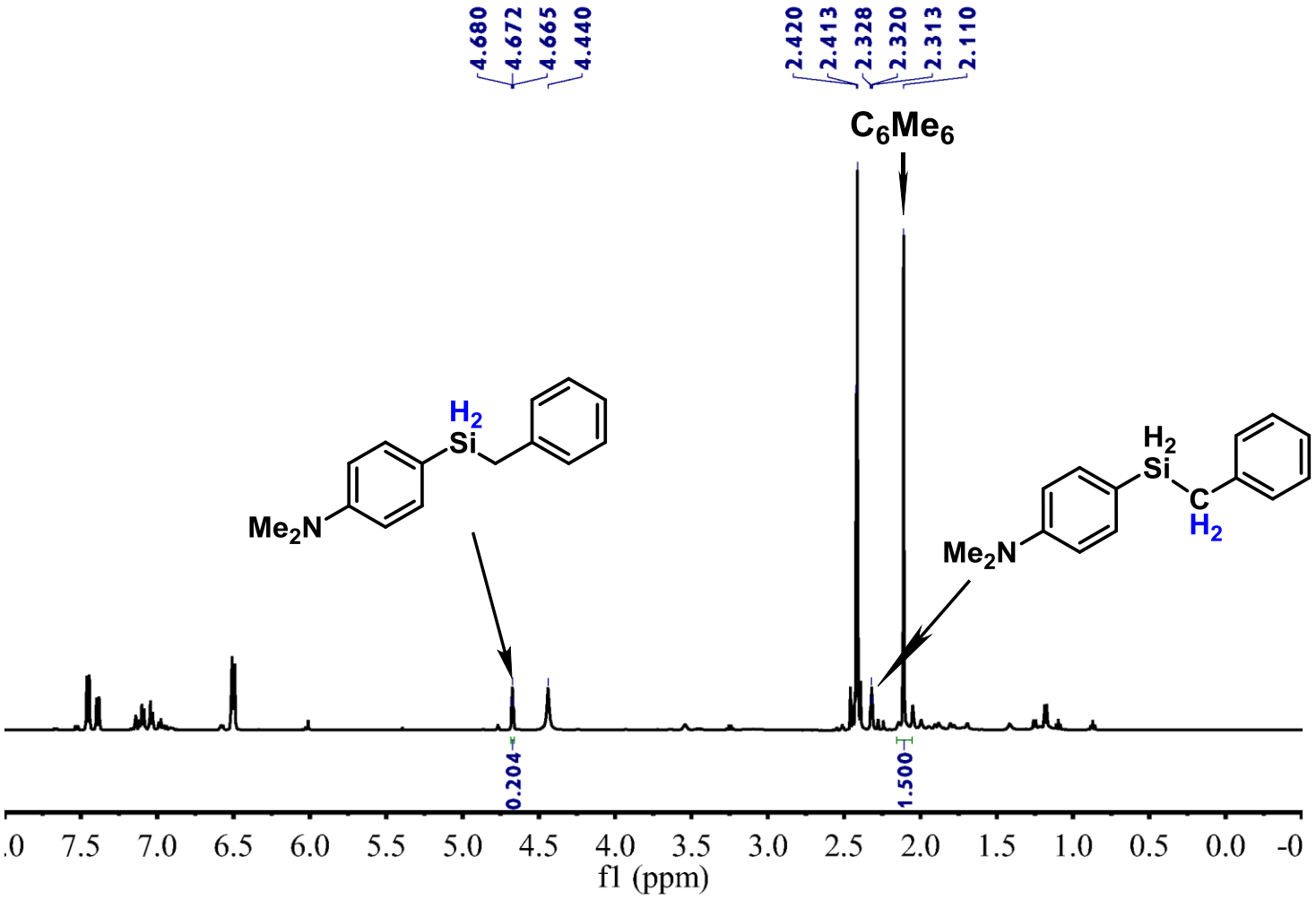

Figure S56. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and 4-NMe_2-$PhSiH_3$ (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

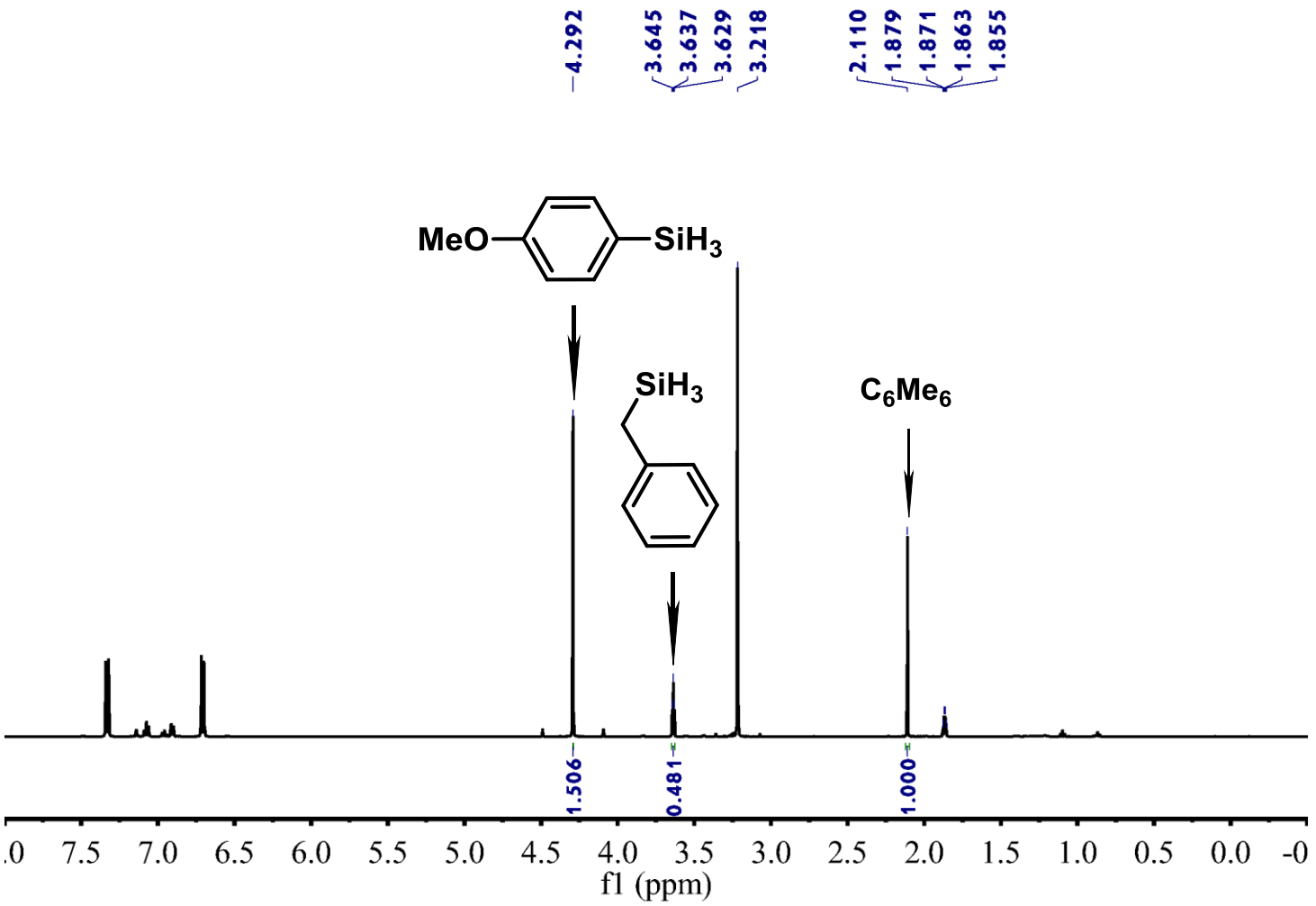

Figure S57. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of benzylsilane and 4-MeO-PhSiH$_3$ (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (500 MHz, C_6D_6, 25 ^{o}C).

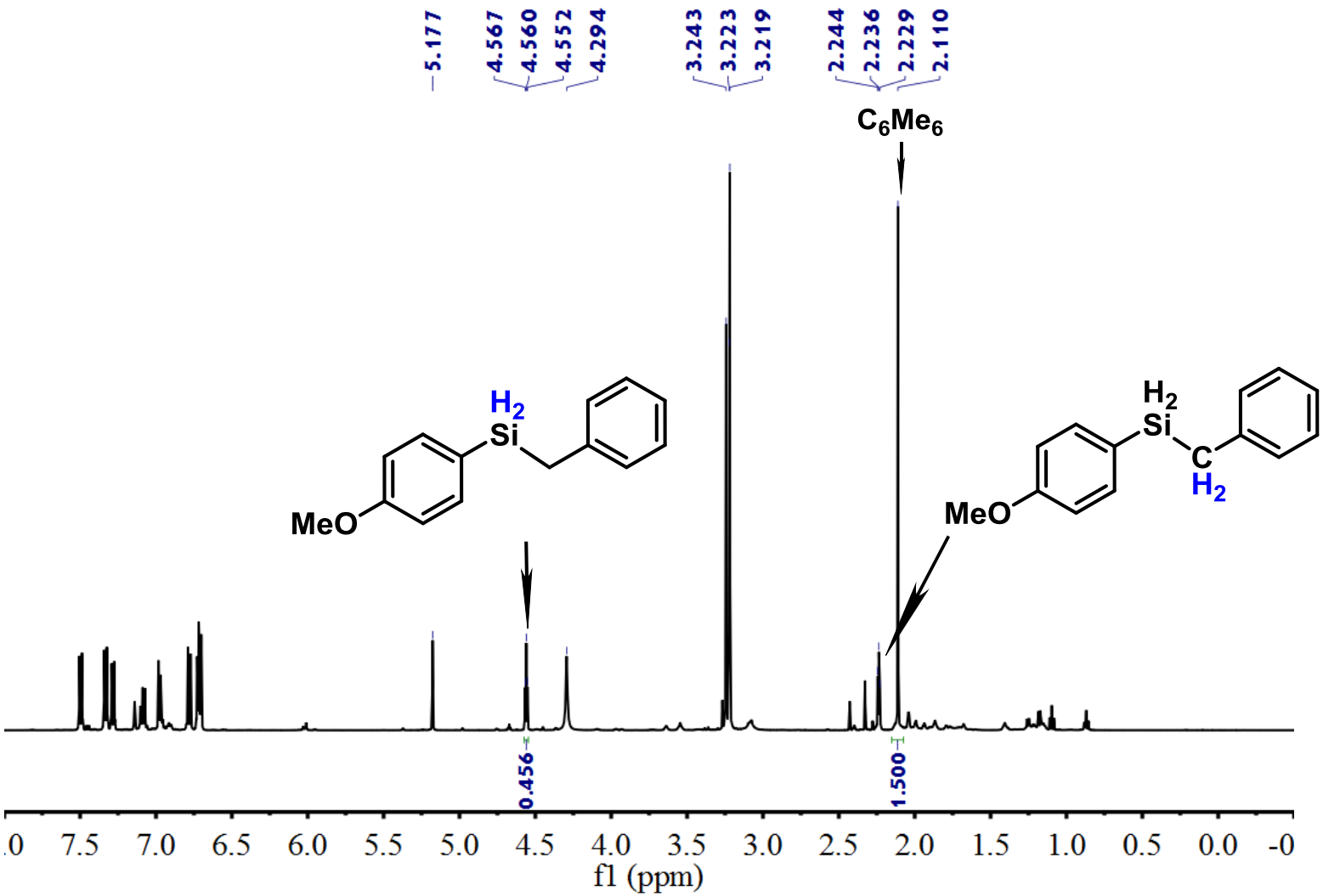

Figure S58. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of benzylsilane and 4-MeO-PhSiH$_3$ (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (500 MHz, C_6D_6, 25 ^{o}C).

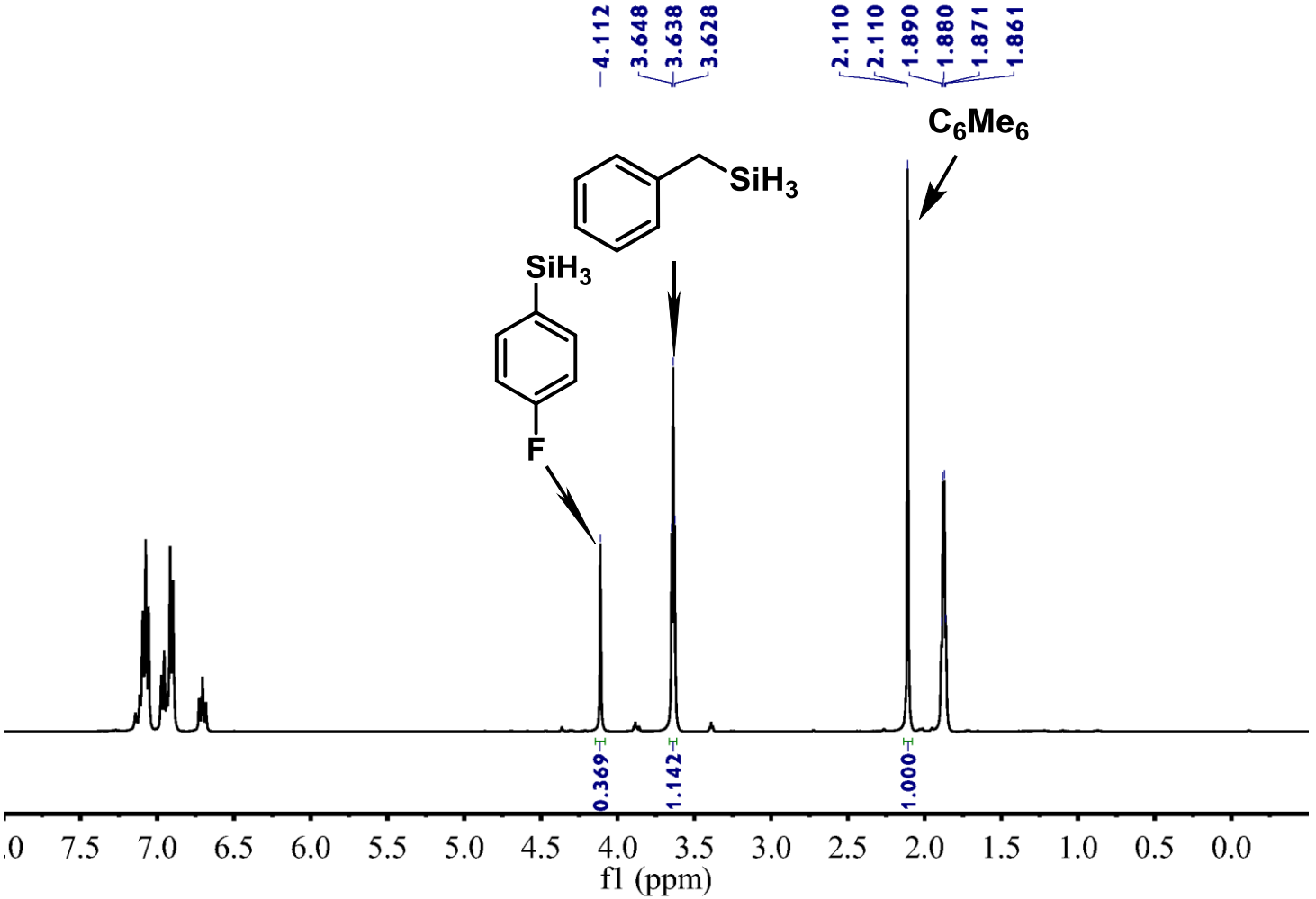

Figure S59. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-F-PhSiH_3 and benzylsilane (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (600 MHz, C_6D_6, 25 ^{o}C).

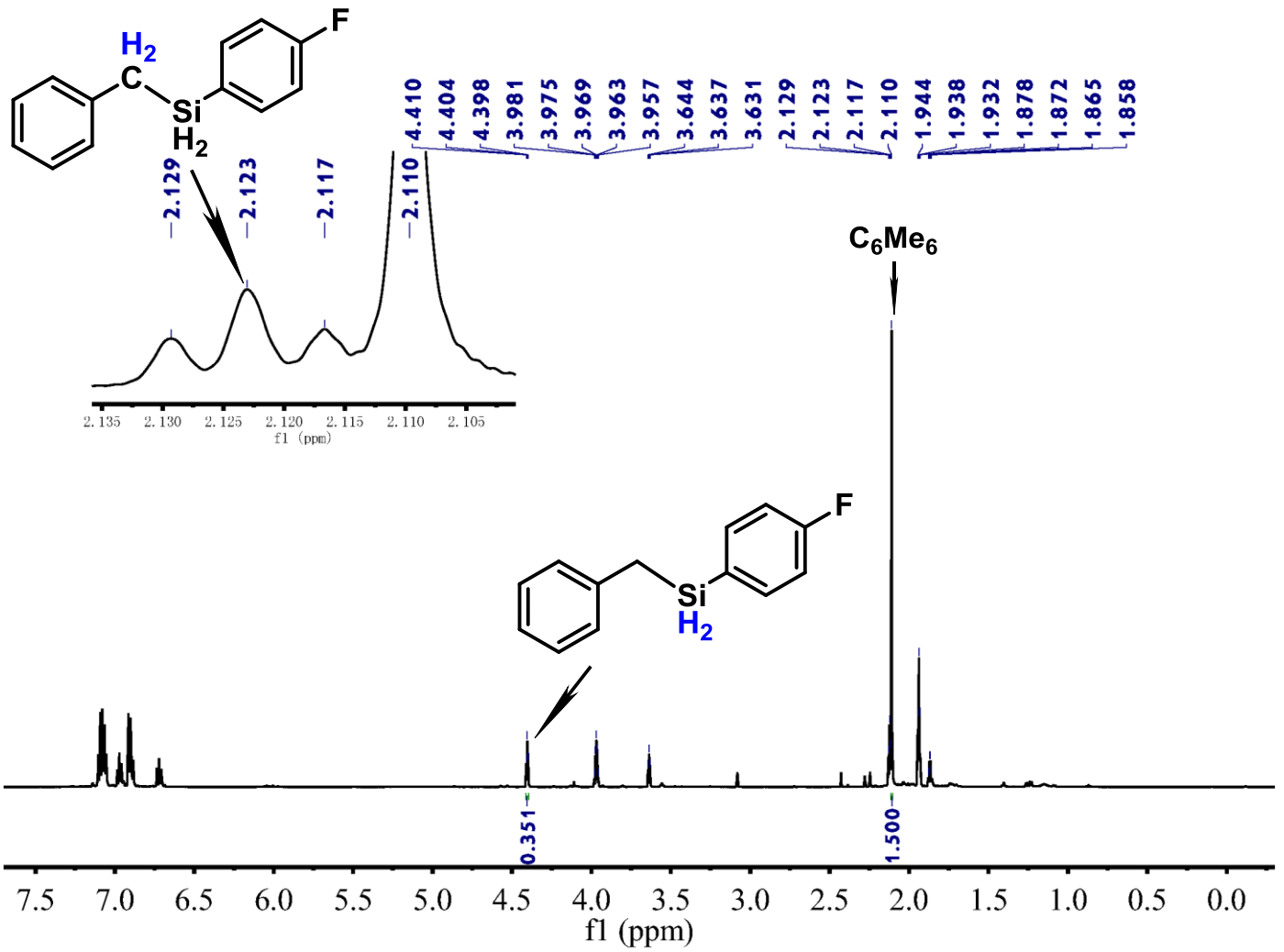

Figure S60. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-F-PhSiH$_3$ and benzylsilane (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (600 MHz, C_6D_6, 25 ^{o}C).

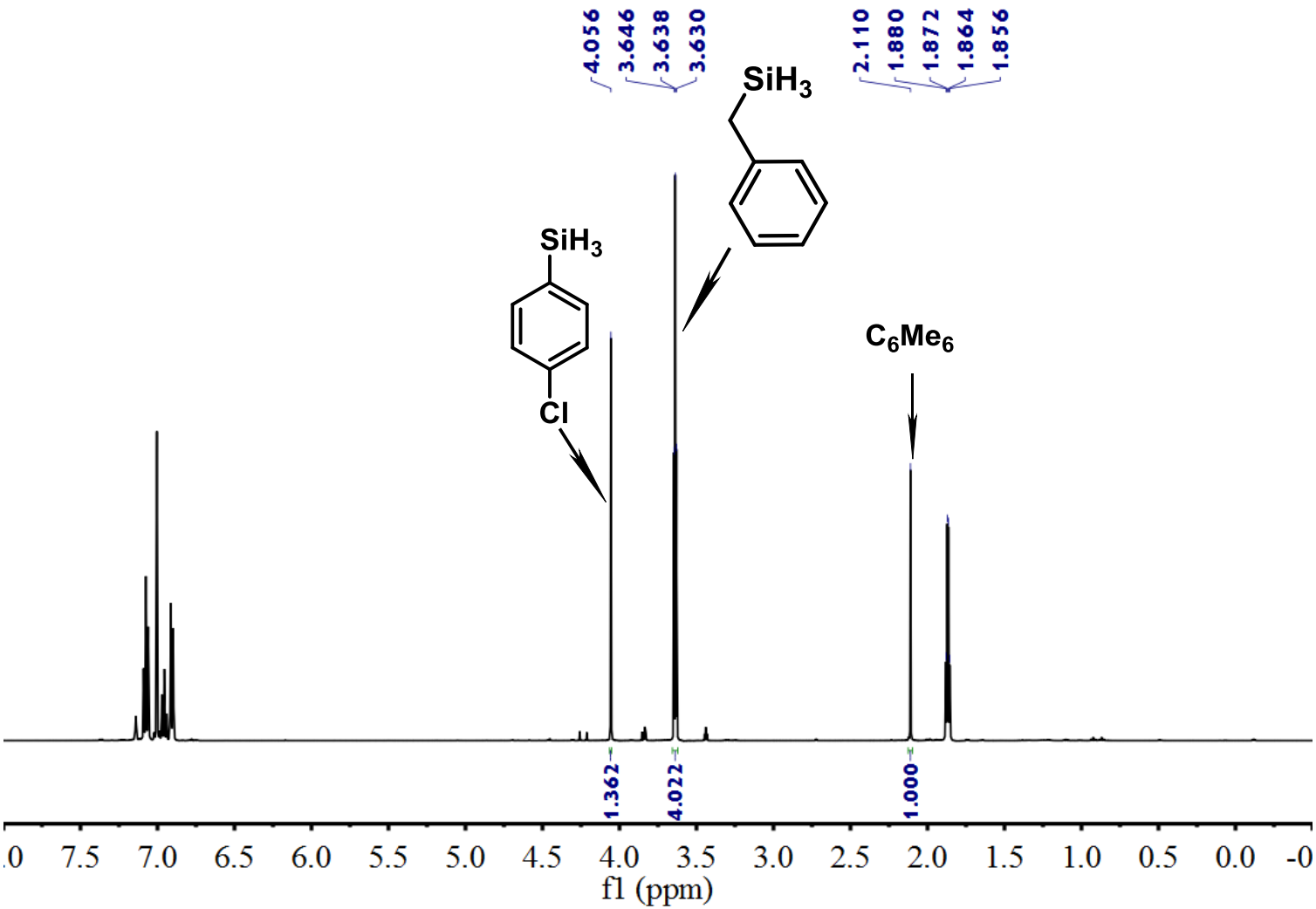

Figure S61. Quantitative ^{1}H NMR spectrum of the C_6D_6 solution of 4-Cl-PhSiH$_3$ and benzylsilane (~3 equiv.) for the cross-desilacoupling catalyzed by **1** with hexamethylbenzene as the internal standard (600 MHz, C_6D_6, 25 ^{o}C).

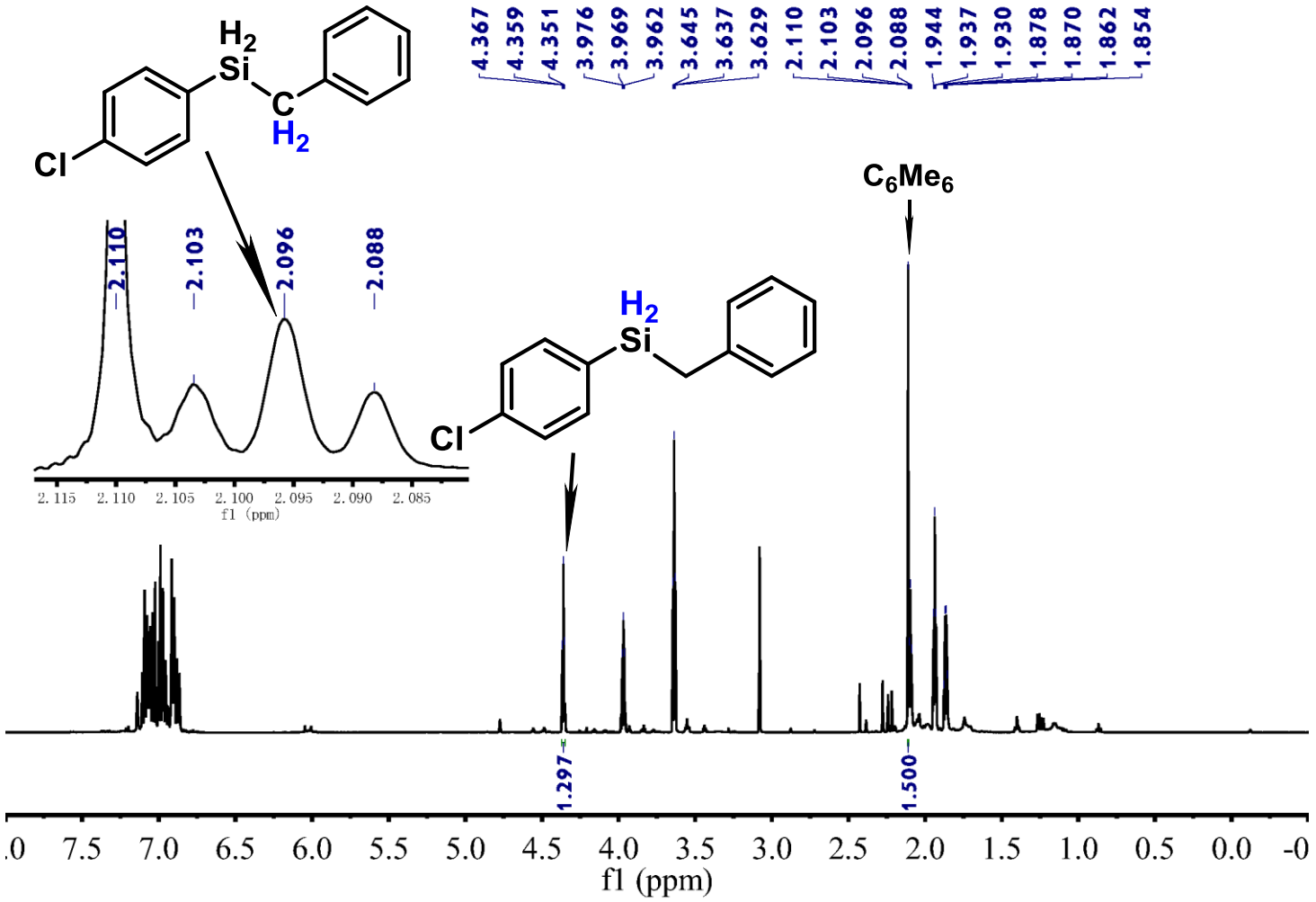

Figure S62. Quantitative ^{1}H NMR spectrum of the products of the cross-desilacoupling of 4-Cl-PhSiH$_3$ and benzylsilane (~3 equiv.) catalyzed by **1** at r.t. in 10 min (Table 3) (600 MHz, C_6D_6, 25 ^{o}C).

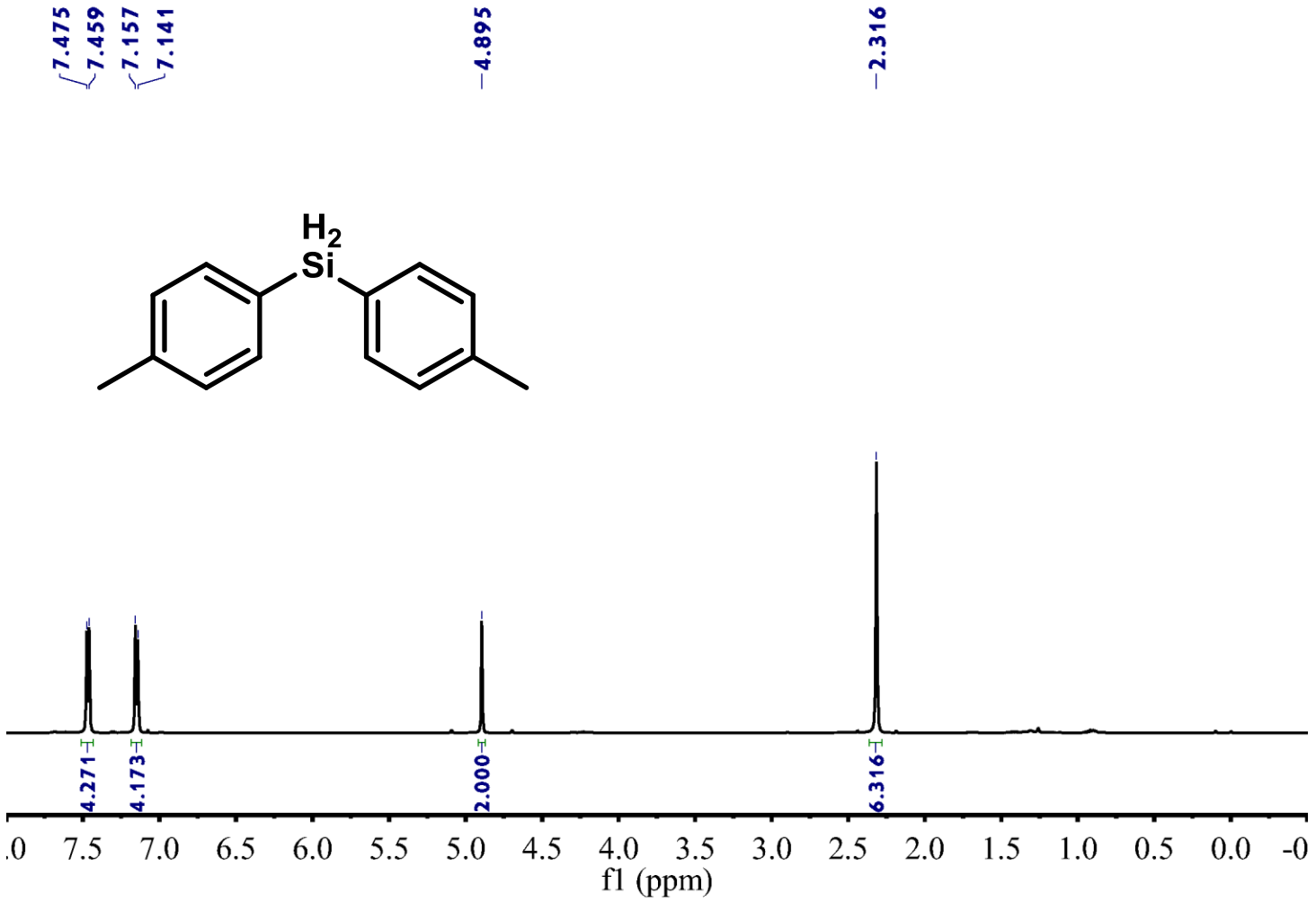

Figure S63. ^{1}H NMR spectrum of dihydrodi(*p*-tolyl)silane (500 MHz, $CDCl_3$, 25 ^{o}C).

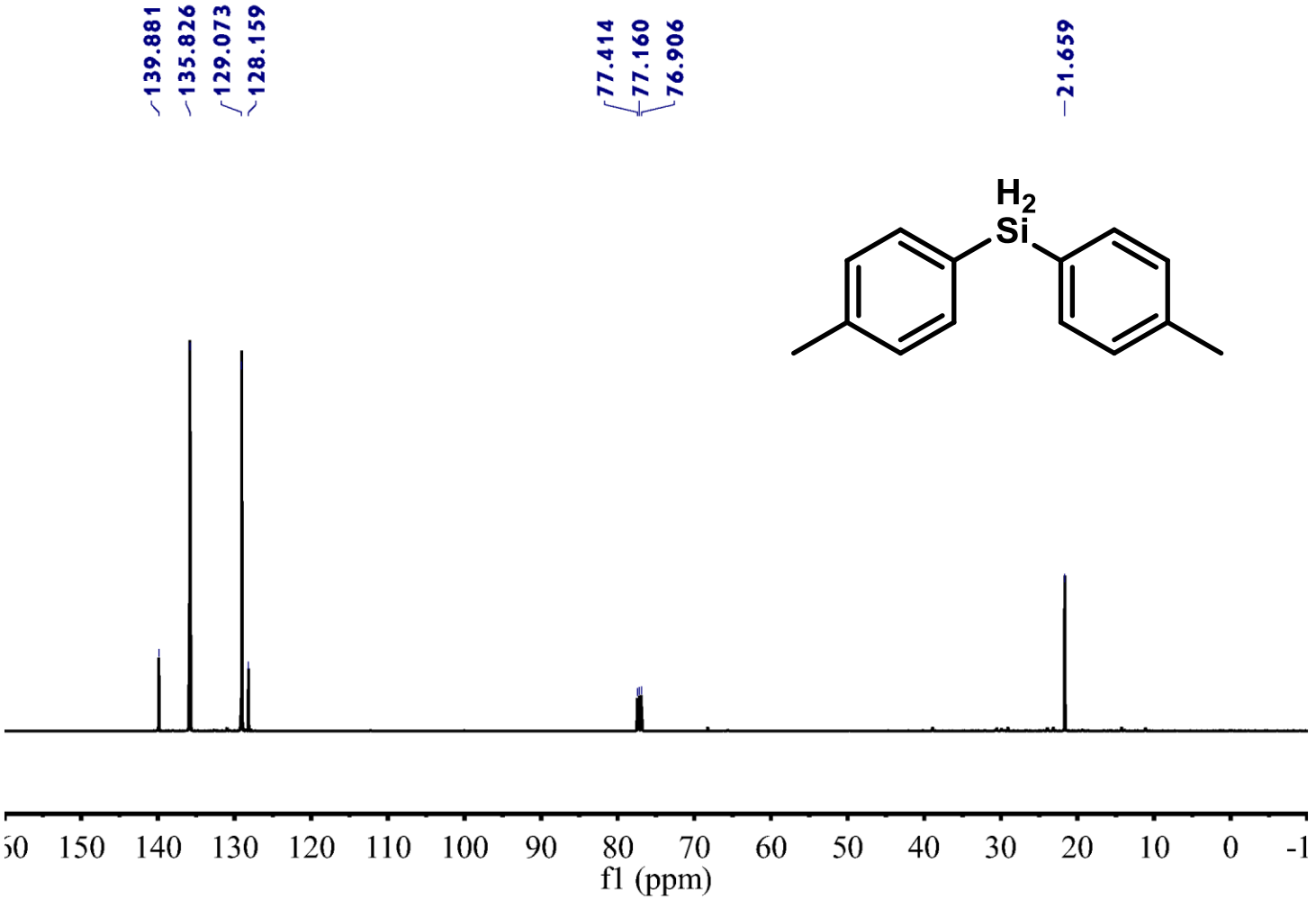

Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of dihydrodi(*p*-tolyl)silane (125 MHz, $CDCl_3$, 25 ^{o}C).

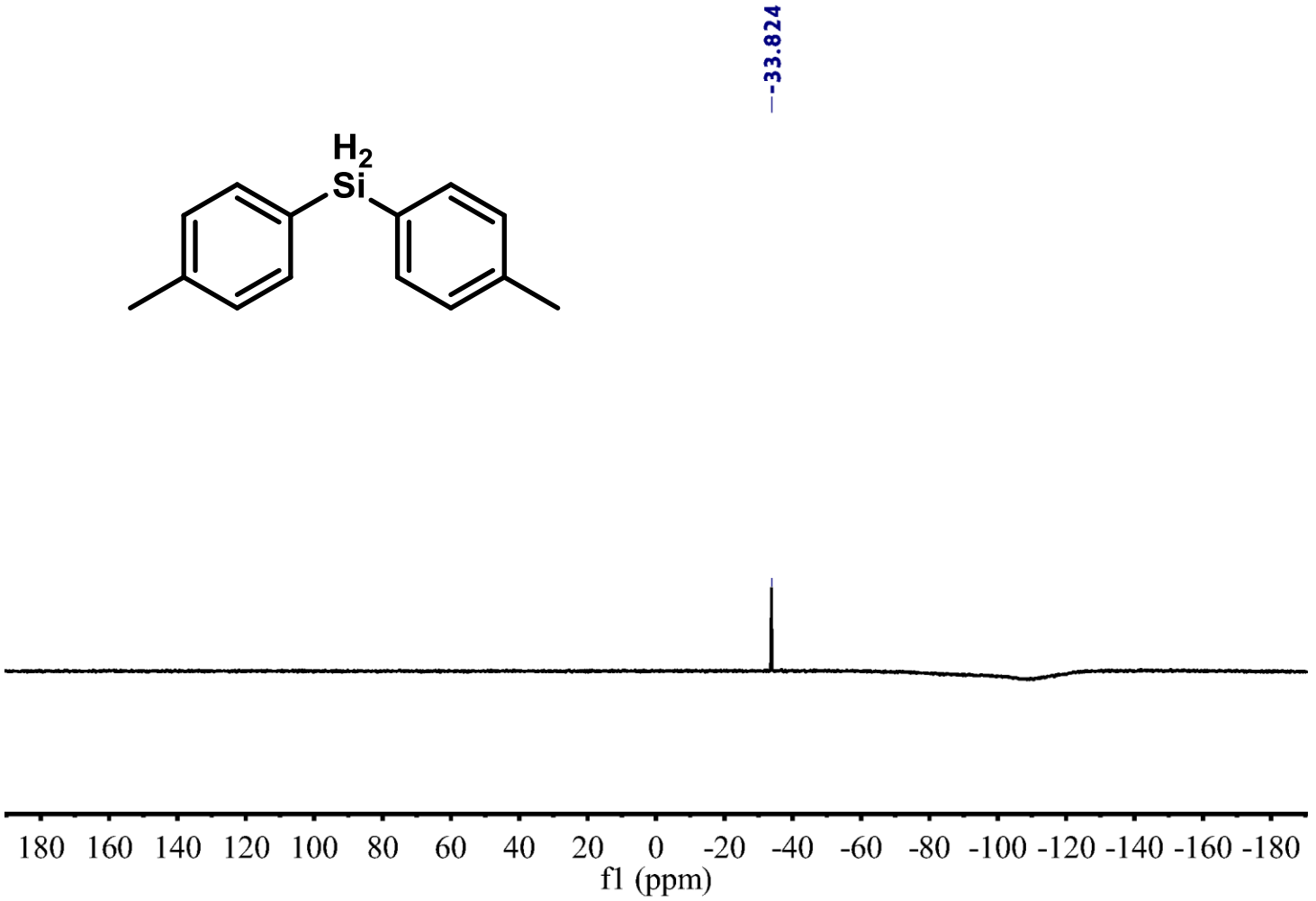

Figure S65. ^{29}Si NMR spectrum of dihydrodi(*p*-tolyl)silane (119.19 MHz, $CDCl_3$, 25 ^{o}C).

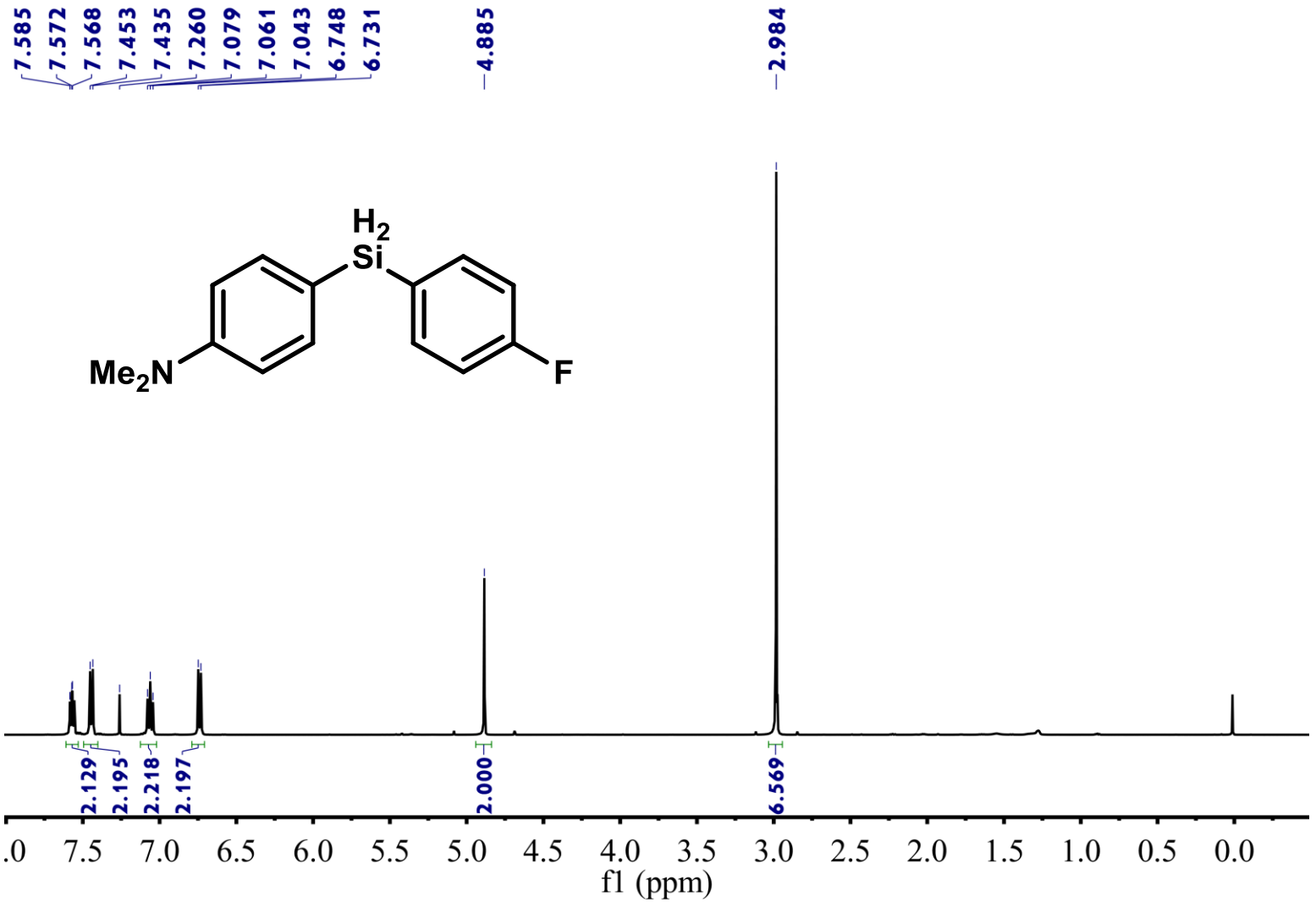

Figure S66. ^{1}H NMR spectrum of 4-(4-fluorophenylsilanyl)-N,N-dimethylaniline (500 MHz, $CDCl_3$, 25 ^{o}C)

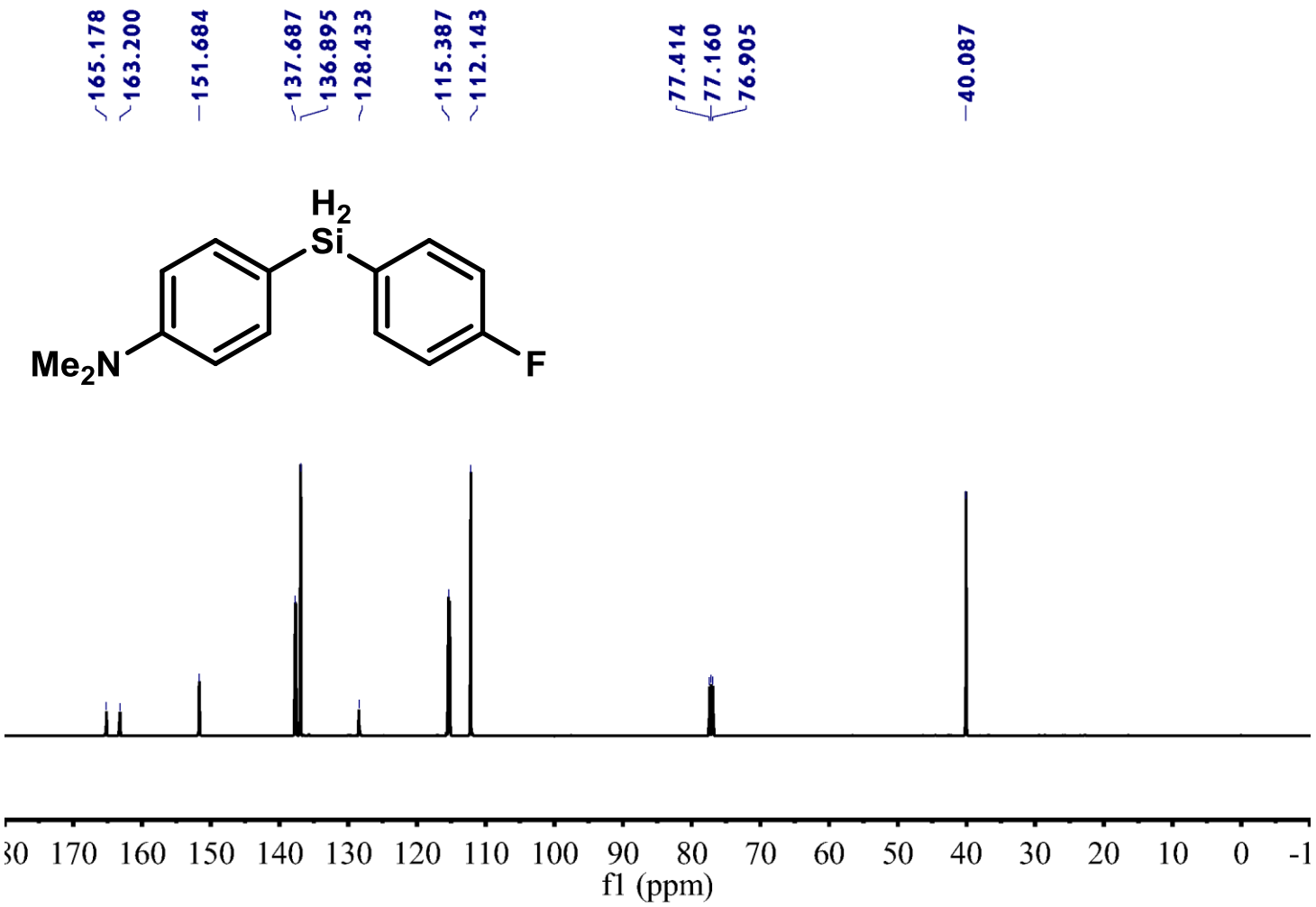

Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of 4-(4-fluorophenylsilanyl)-N,N-dimethylaniline (125 MHz, $CDCl_3$, 25 ^{o}C).

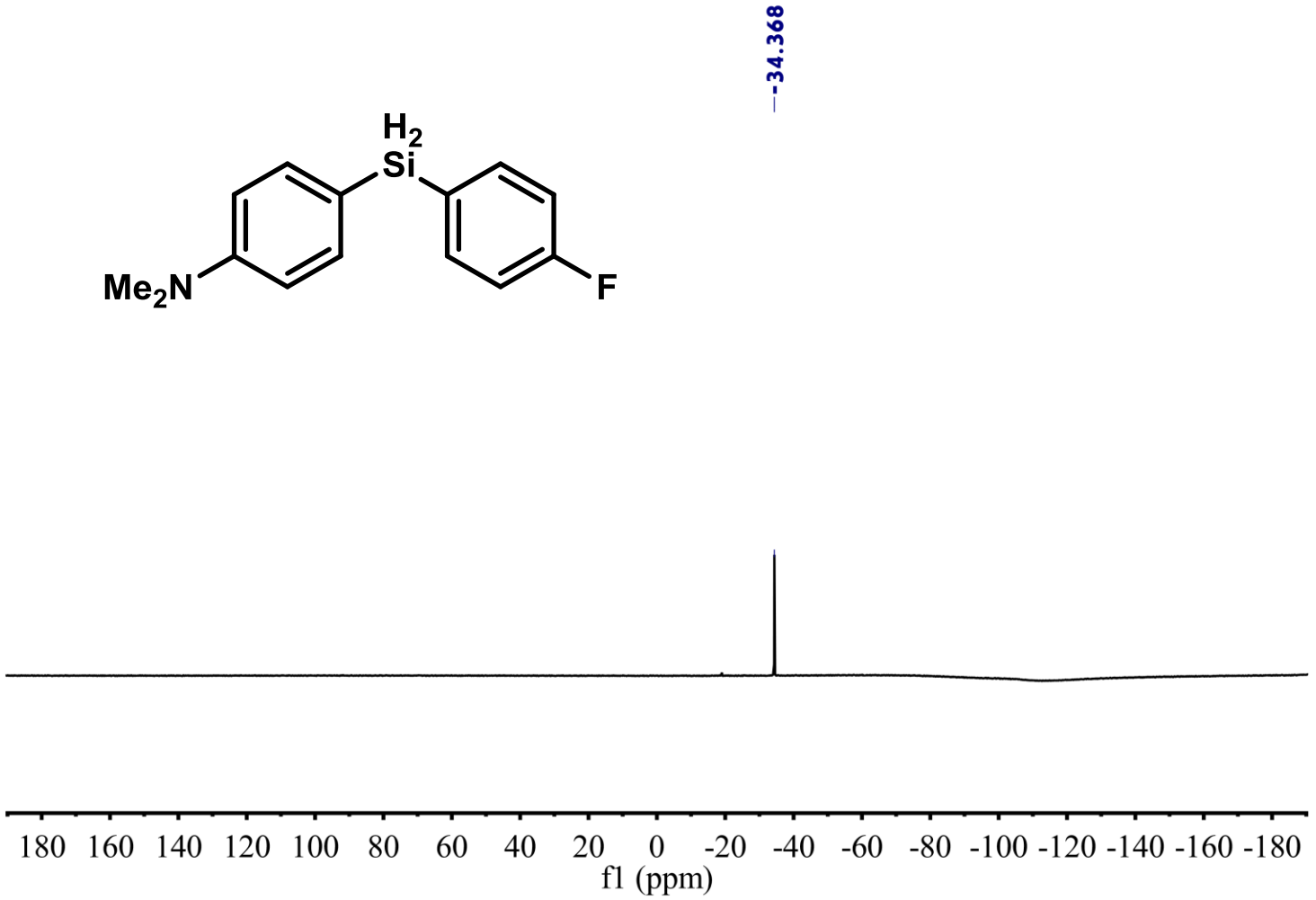

Figure S68. ^{29}Si NMR spectrum of 4-(4-fluorophenylsilanyl)-N,N-dimethylaniline (119.19 MHz, $CDCl_3$, 25 ^{o}C).

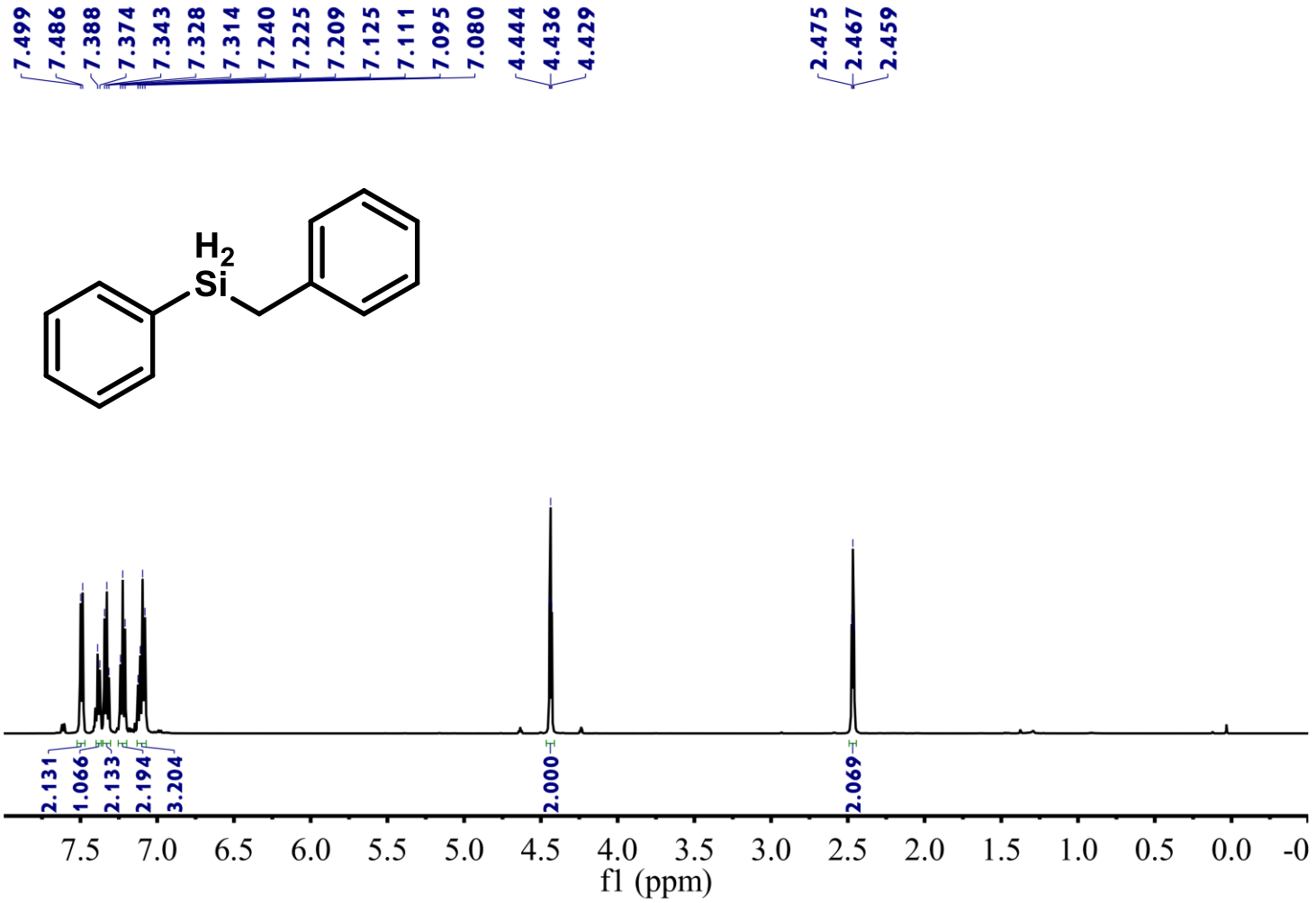

Figure S69. ^{1}H NMR spectrum of benzyl(phenyl)silane (500 MHz, $CDCl_3$, 25 ^{o}C).

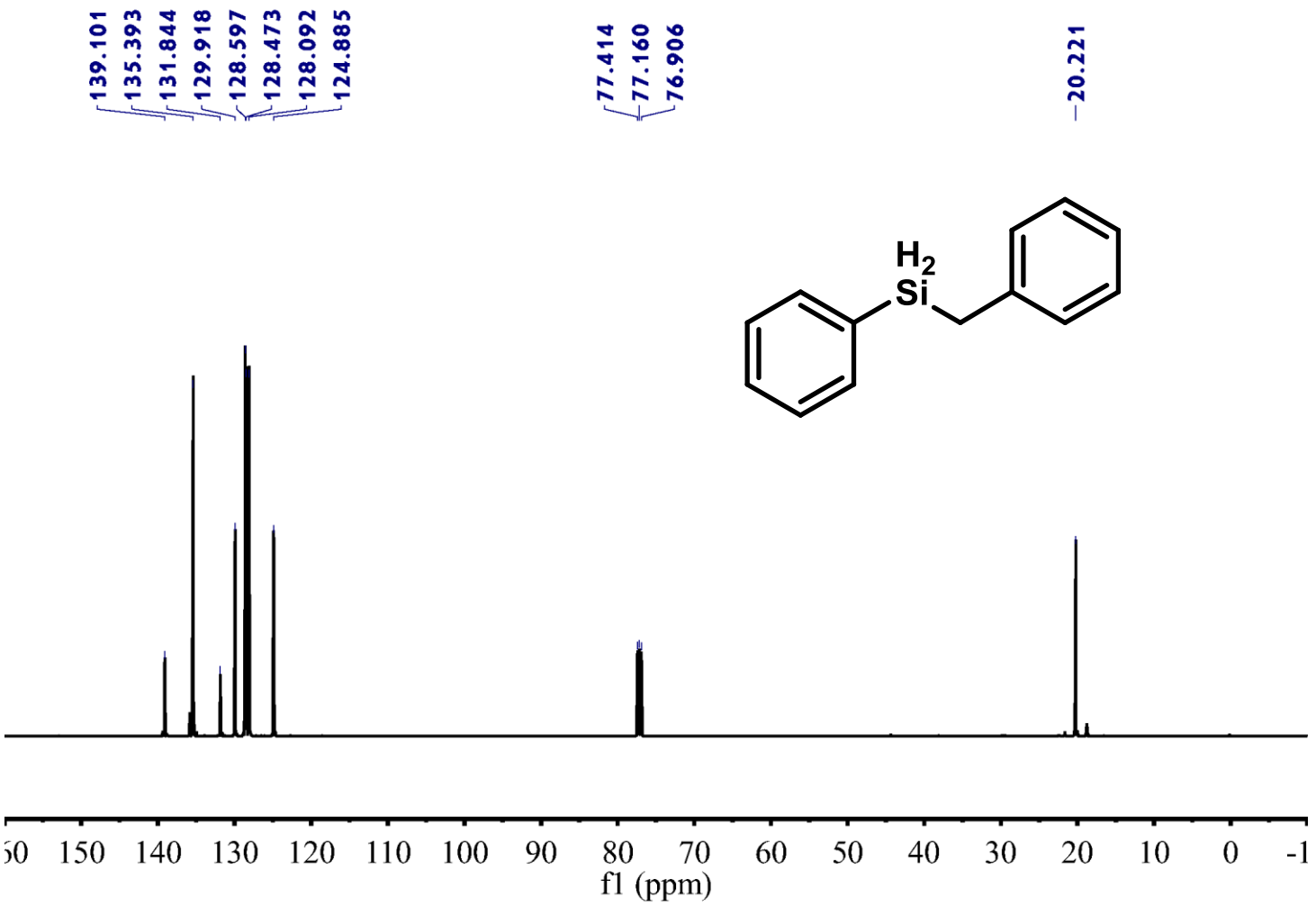

Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of benzyl(phenyl)silane (125 MHz, $CDCl_3$, 25 ^{o}C).

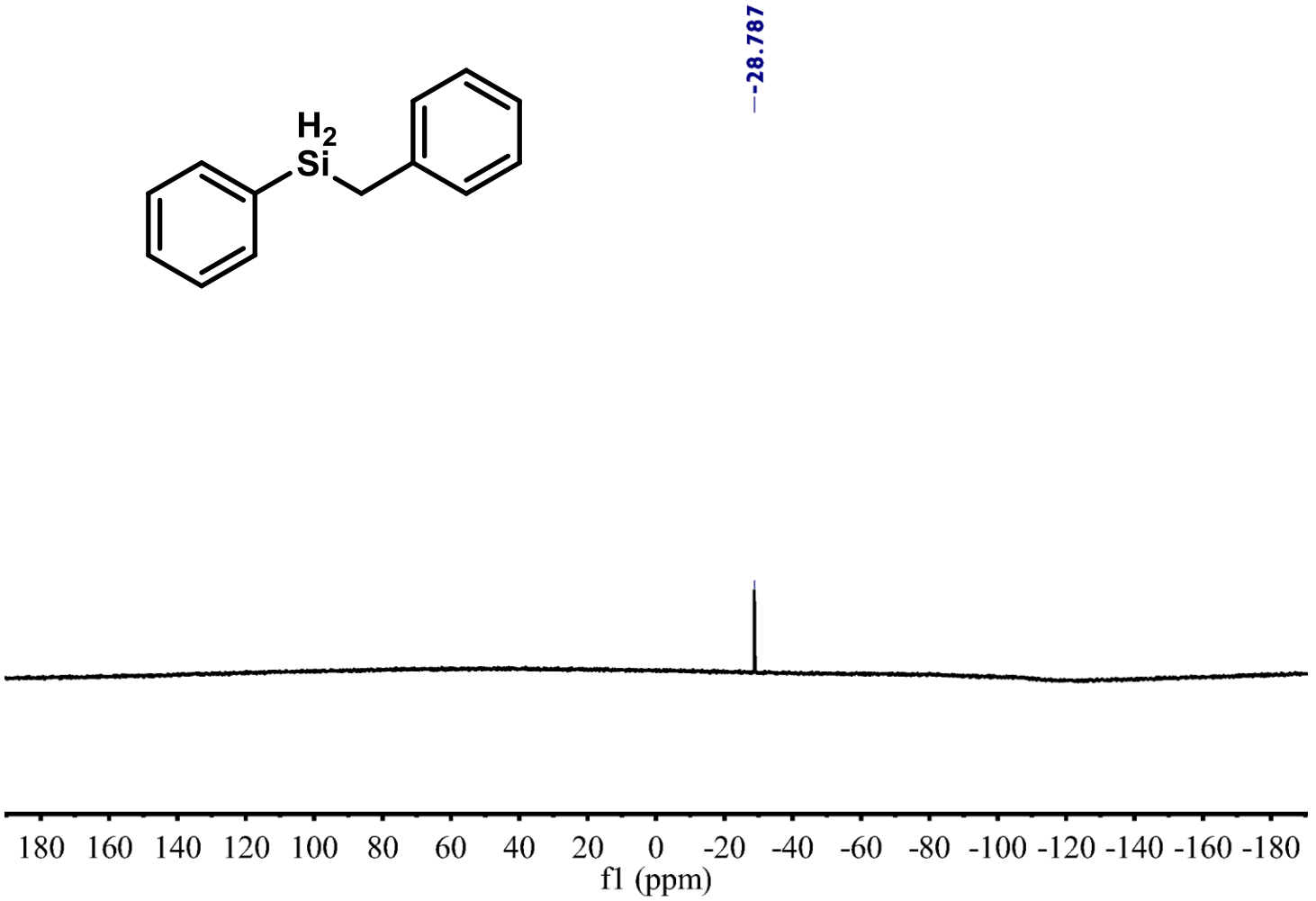

Figure S71. ^{29}Si NMR spectrum of benzyl(phenyl)silane (119.19 MHz, $CDCl_3$, 25 ^{o}C).

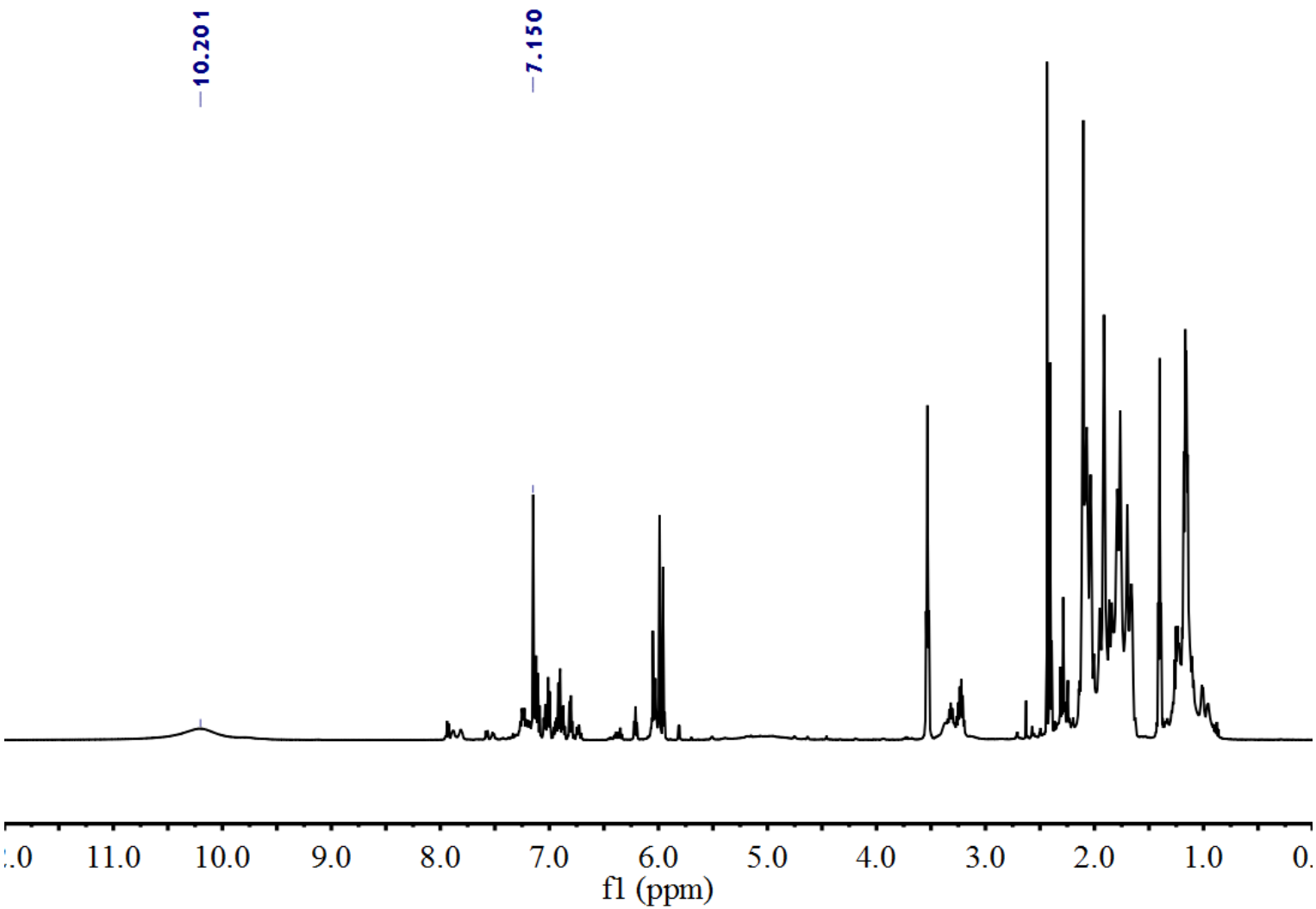

Figure S72. ^{1}H NMR spectrum of stoichiometric reaction of complex **1** with $PhSiH_3$ (500 MHz, C_6D_6, 25 ^{o}C).

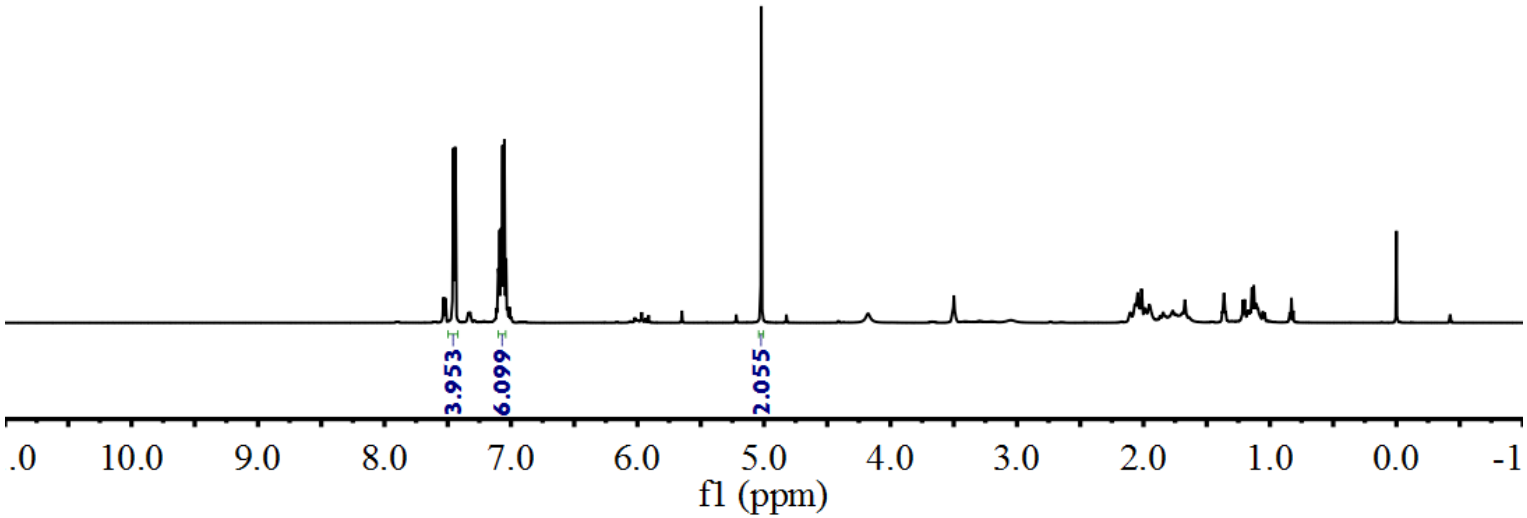

Figure S73. ^{1}H NMR spectrum of the products of redistribution of $PhSiH_3$ catalyzed by 2.5 mol% of **2** at r.t. in 10 min (500 MHz, C_6D_6, 25 ^{o}C).